

Theory and Applications of Transport in Porous Media

Vyacheslav G. Rumynin

Subsurface Solute Transport Models and Case Histories

With Applications
to Radionuclide Migration



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With Applications to Radionuclide Migration

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Preface

Studies of solute fate and transport in the subsurface environment have been playing a significant role in hydrogeology over the past half century. The problem directly relates to the quality of natural water resources, which are essential to all kinds of life, and are a basic element in many sectors of human society. Most migration studies of both natural and anthropogenically derived species have considered the motion of a fluid (groundwater) accompanied by diffusion–dispersion phenomena, physicochemical interactions, as well as microbiological transformations, known to be the dominant factors providing the impact of contaminants upon groundwater supplies.

Over the last decades, essential progress in the migration process description has been achieved due to the development of mathematical background and numerical methods and laboratory and field investigations of particular transport mechanisms and physicochemical interactions. However, in many real situations, the subsurface material heterogeneity and variations in fluid properties, resulting in nonlinear contaminant plume behavior, make the prediction accuracy of the transfer processes too low to satisfy the practical needs. The lack of comprehensive field studies of solute movement is often cited as a major impediment to our understanding of solute transport in such systems.

Therefore, this work is aimed at the development of the basic knowledge of the subsurface solute transfer with a particular emphasis on field data collection and analysis coupled with modeling (analytical and numerical) tool application. The book is based mostly on field materials from author's long-standing, recent, and current experience in the study of groundwater quality related problems. The diversity of these problems is concerned with the variety of geological settings as well as the anthropogenic effects and processes caused by human activity. Some problems encountered in practice looked as challenge-like and, thus, the author was encouraged to search for new solutions and approaches. The relevant theoretical developments are concerned mainly with the formulation and solution of deterministic mass-transport equations for a wide range of engineering issues in groundwater quality assessment and forecasting that can be of some interest for bridging the gaps still existing in our knowledge of contaminant hydrogeology.

The book gives many computation examples and case studies drawn from the conducted field investigations. Those examples show the applicability of the theory

and methods for solving various practical problems and making decisions in contaminant hydrology to explain the observed and to forecast the future groundwater quality. The analyzed problems are as follows:

- (1) investigation and prediction of groundwater contamination by industrial contaminants and solutions (radionuclides, chloride and nitrate brine) with special focus on the effect of (a) aquifer heterogeneity, anisotropy, and dual porosity, (b) density contrast between industrial waste and groundwater, (c) physico-chemical interactions that play a major role in retarding (e.g., adsorption) or enhancing (e.g., interactions between dissolved species and mobile colloids) contaminant transport;
- (2) prediction of the effects of pumping on groundwater quality at wellfields: (a) the displacement of stratified initial concentration in artesian and coastal (off-shore) groundwater systems due to water pumping, (b) downward movement of mineral-weathering products in the vadoze zone (above the lowering water table) with water recharge to the producing aquifers;
- (3) groundwater dating using stable and radioactive isotopes for prediction and assessment of contamination potential and the time that would be needed to displace contaminants from the groundwater system;
- (4) field and laboratory tests' design and analysis, and monitoring data interpretation;
- (5) partitioning of surface and subsurface flows using isotope technique;
- (6) formation of evaporated salt deposits in closed surface water reservoirs having a hydraulic connection with the surrounding groundwater systems.

Several parts of the book demonstrate the potential for using numerical groundwater flow and transport models in environmental risk assessment of subsurface contamination by dense or light miscible liquid waste. Environmental isotope data were utilized for defining the groundwater systems and modeling data analysis. However, numerical modeling emerged in the book mostly as one of the primary tools used to understand the most important physical and physicochemical processes that occur in groundwater systems, as well as for getting analytical approximations for some coupled problems, which do not necessarily have exact solutions in closed analytical forms or cannot be treated with the classical methods.

One of the most essential topics addressed in the book is the migration and fate of radionuclides. Model development is motivated by field data analysis from a number of radioactively contaminated sites in the Russian Federation: near-surface radioactive waste (RW) disposal sites in northwestern Russia and the Southern Urals, and two deep-well RW injection sites in Western Siberia. These sites are part of huge nuclear industry enterprises licensed to possess radioactive materials and also involved in hazardous-waste operations, which are supervised by RosAtom, the State Nuclear Energy Corporation, Russian Federation.

The total activity of radionuclides that were released (accidentally or intentionally) in aquifers at many sites reaches hundred thousands to hundred millions Ci. Any of the three RW disposal sites out of the four mentioned here (located in Southern Urals and Western Siberia) probably contains more radioactive contamination

in the subsurface than any other site in the world. Additionally, detailed information on physical, mechanical, and solute transfer properties of clay formation (which is considered as a host medium for the engineered underground RW repository in the northwestern part of the Russian Federation) is also analyzed.

Those sites play a unique role in the advancement of knowledge of the subsurface behavior and fate of many hazardous radionuclides and can be considered as field-scale laboratories. The book is focused on the modeling and analytical assessments of a range of physical and chemical processes and interactions of concern. Some of the key issues needed to be addressed included:

- (1) study of the behavior of a broad spectrum of radionuclides (fission products and actinides) in waste (with low content of dissolved solids and brine) based on long-term (up to 50 years) monitoring data in shallow and deep aquifer systems;
- (2) study of the spatial variability of migration properties of aquifer materials and clayey semipervious formations;
- (3) assessment of the role of brine-induced advection in redistribution of radioactive components at waste disposal sites;
- (4) study of adsorption hysteresis implying isotherm nonsingularity and other non-ideal sorption phenomena, as well as the assessment of their role in natural attenuation of radioactively contaminated sites;
- (5) analysis of transient hydrogeochemical-barrier effects, facilitating radionuclide transport, and some other mechanisms responsible for “fast” radionuclide transport in aquifers;
- (6) experimental evidence for colloid-facilitated radionuclide (actinide) transport, and mathematical description of the phenomena.

The model developments were accompanied by laboratory studies into natural attenuation, radionuclide adsorption and desorption kinetics and equilibrium (including when colloidal particles are involved). Batch tests were conducted with different radioactive solutions under different temperature and pressure conditions. Anomalous behavior of radionuclides was observed and modeled.

This study can be regarded as the continuation of a series of works started by the author in the 1970s in cooperation with the outstanding Russian scientist, hydrogeologist, V.A. Mironenko, whose contribution to the development of several lines of studies in hydrogeology and hydrogeomechanics is difficult to overestimate. At the same time, this book could not have appeared were it not for the all-round support from colleagues – researchers from E.M. Sergeev Institute of Environmental Geology, St. Petersburg Division, RAS, and St. Petersburg State University, who rendered assistance in the preparation of parts of the book. In this connection, the author very much appreciates the help of Leonid Sindalovsky in implementation of many numerical algorithms considered in the book, the contribution of Pavel Konosavsky to the joint studies of adsorption hysteresis and the development of some models of solute transfer in the porous media under disturbed flow conditions. The author also appreciates Igor Tokarev’s willingness to share his data on regional isotope study of a groundwater system in the area of RW disposal at Tomsk-7 site.

The study discusses experiments carried out in laboratories of A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, RAS, and A.P. Alexandrov Technical Institute under supervision of Drs. Elena Zakharova, Elena Kaimin, and Elena Pankina. The author expresses his sincere gratitude to these groups for cooperation that have yielded new results.

The author appreciates the cooperation of Aretech Solutions and TIHGSA Enterprises allowing him to learn new hydrogeological aspects related to the formation of groundwater resources and quality in arid regions.

The author also much appreciates the attention to his work and fruitful discussions with Profs. Vsevolod Shestakov and Sergey Pozdniakov, Moscow State University, and Dr. Andrei Zubkov, the head of the Environmental Protection Division (Siberian Chemical Plant), and many other brilliant experts—hydrogeologists, whose talent and enthusiasm in scientific and production work allows the author to believe in the future of the Russian hydrogeological school.

Many efforts were made by Dr. Chin-Fu Tsang and Prof. Jacob Bear to organize this work in a proper way in order to prepare the book in a format acceptable for the international publishing company, Springer. Discussions and exchange of information, ideas, and opinions with them was a great support to this work.

Finally, the author very much appreciates the help of Dr. Gennady Krichevets in professional translation of the book and many useful comments from him allowing the author to make certain improvements to the book. The author would also like to acknowledge the help of Ekaterina Kaplan for her editorial assistance and technical support of the work.

Thus, the book, along with theoretical findings, contains field information, which will facilitate the understanding of subsurface solute transport and the development of a methodology for practical application to groundwater hydrology. This book addresses scientists and engineers who are interested in the quantitative approach to studying groundwater migration processes. The book can also be profitably read by students.

December 28, 2010

Vyacheslav G. Rumynin

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Part I

The Essentials of Dissolved Species Transport in the Subsurface Environment: Basic Definitions, Fundamental Mechanisms and Mathematical Formulation

The theory of solute migration in groundwater originates from studies devoted to the description of elementary pore-scale mechanisms (processes) of the movement of dissolved species in a single fluid phase, including advection, molecular diffusion, and hydrodynamic dispersion, which are accompanied by acts of simplest sorption-type physicochemical interactions and solute decay (destruction) reactions. Those studies were mostly based on the classical theory of fluid motion in idealized porous media ([Muskat 1937](#); [Scheidegger 1957](#)), as well as on chemical kinetics and reaction engineering. However, it has become clear that there exist some specific features in the application of conventional hydrodynamics methods to the formulation, solution, and analysis of many practically significant hydrogeological problems. In particular, the relative significance of those mechanisms and interactions in the general migration process was soon found to depend on the spatial and temporal scale of their analysis, the lithological and genetic type of geological sections, and the spatial correlation structure of their physical parameters, the structure of water flows, and the conditions on their inner and outer boundaries. This, as well as the specific features of the application of physico-mathematical apparatus to the solution of appropriate boundary problems regarding dissolved species transport in single-phase constant-density groundwater flows, will be the focus of the first part of this book.

Mathematical models used to describe solute transport in the unsaturated zone of the subsurface are also included in this part of the book. As will be shown, for accurate prediction of contaminant transport through the unsaturated zone, field equations for transport of moisture and chemicals must be coupled.

The equations given here represent a deterministic approach to describing the subsurface transport phenomena, and have been assembled from a considerable collection of previous works and investigations conducted by many recognized

authorities in the field of subsurface fluid dynamics. More generalized fluid flow and transport models, accounting for the stochastic nature of aquifers and soil materials are subject of high profile, well-publicized special investigations.

The proposed material forms a bridge to the understanding of solute transport under near-natural conditions and the analysis of migration of complex-composition solutions (liquids) whose properties differ from those of formation waters. Besides, the approaches developed here will be used to assess the contributions of various physicochemical processes, which in many cases control the potential of anthropogenic impact on groundwater quality under natural conditions.

Chapter 1

Advection and Dispersion of Dissolved Species in Aquifers

The transfer of chemical components that, when in solutions, have no effect on the physical properties of aquifer materials and groundwater, is inseparable from the groundwater flow. Their advective transport involves micro- and macrodispersion processes, which control the extent of solute dispersion in homogeneous and heterogeneous aquifers. In this chapter, we will consider the migration models that describe the motion of solutions miscible with groundwater in homogeneous aquifers. The solute migration processes in heterogeneous (stratified and fractured-porous) systems will be discussed in separate chapters.

1.1 Governing Equations and Solute Transport Parameters

The traditional description of flow and solute transport in natural porous and fractured media (soils, sediments, rocks), as well as the solution of the majority of subsurface hydrology problems, are based on the continuum mechanics approach (Bear 1972; Shestakov 1995; Bear and Cheng 2010). The continuum assumption considers the fluid and solid phase as a continuous medium with flow and solute (mass) transport parameters taken to be well-defined at the REV (representative elementary volume) scale. The appropriate level of statistical averaging of medium properties is a priori attained in complexes of weakly lithified porous sediments. The construction of solute migration models in fractured rocks requires the validity of medium's continuity assumption, REV, to be analyzed more thoroughly and the possible scale effects associated with the "structuring" of groundwater flows in fracture space to be taken into account in the models (Schwartz et al. 1983; Berkowitz 2002; Kosakowski 2004; Neuman 2005; Reeves et al. 2008a, b). Effective (or equivalent) continuum models utilizing REV approach may not be applicable for real fractured rocks (see below).

The mathematical formalization of the subsurface migration is based on the groundwater flow continuity equation (which is equation of conservation of mass), Darcy's law and the solute transfer equation together with an appropriate set of boundary and/or initial conditions. This section is devoted to analysis of such models.

1.1.1 Advection of Conservative Components in Porous and Fractured Media

Advection of particles or heat, from the classical fluid-dynamical point of view, is the transfer of matter or heat by the flow of a fluid. Advection due to the fluid's bulk motion in pores or fractures is among the major mechanisms governing solute transport in aquifers lying in the hydrodynamic zone of active water exchange. The driving force for advection is the gradient in the hydraulic head.

In unconsolidated granular porous media, this process proceeds in practically nonstructured void space; whereas liquid motion in fractured rocks, consisting of an assemblage of intact rock blocks (matrix) separated by intersecting sets of joints, proceeds in the space which generally has a distinct structure. In some cases (primarily, when the process is considered at a local scale), these distinctions require differentiation of the computation schemes (models) used to describe solute migration in two types of rock formations with different nature of void space.

1.1.1.1 Flow Field and Actual Fluid Velocity

In subsurface fluid dynamics, flow velocity field, creating potential for advection of dissolved solutes is a vector field. This field can be mathematically described by a continuity equation written in the most general form for compressible pore-fluid mixtures as follows

$$\frac{\partial \phi \rho}{\partial t} + \nabla \cdot (\rho \mathbf{q}) = 0, \quad (1.1)$$

where $\mathbf{q}$ is the specific discharge or *Darcy velocity* (a vector with 3 components) [LT^{-1}],

$$\mathbf{q} = -\frac{\mathbf{K}}{\mu} (\nabla P - \rho \mathbf{g}); \quad (1.2)$$

ρ is the liquid density [ML^{-3}]; ϕ is the porosity defined as the void space between grains (in porous-type formations) or fracture walls (in consolidated rocks) filled with water [L^3L^{-3}]; P is the hydraulic pressure; $\mathbf{K}$ is the permeability [L^2] (second-order tensor with 9 components, three of which are K_x , K_y , K_z); μ is the dynamic viscosity [$\text{ML}^{-1}\text{T}^{-1}$]; $\mathbf{g}$ is the gravity vector [LT^{-2}]. The term $\nabla \cdot (\rho \mathbf{q})$ is called the divergence of fluid flux, representing the net fluid influx/efflux through the element and sometimes is written as $\text{div}(\rho \mathbf{q})$. Equation 1.1 does not include the inflow/outflow source-terms.

The first chapters of this book deal with calculating the motion of components whose concentration C has no effect on the density ($\rho = \text{const}$) and viscosity ($\mu = \text{const}$) of liquid in the pores (fractures). The possible initial ($t = 0$) variations of groundwater density are also neglected. The pores are assumed to be filled with

water alone: no other liquids or gas phase are present. In such case, Eqs. 1.1 and 1.2 can be rewritten in terms of hydraulic head, h (Bear 1972, p. 207),

$$S_s \frac{\partial h}{\partial t} + \nabla \cdot \mathbf{q} = 0, \quad (1.3)$$

$$\mathbf{q} = -\mathbf{k} \nabla h, \quad (1.4)$$

where S_s is the specific storage of the porous medium [L^{-1}], which is the volume of water, dV_w , that a volume of an aquifer, dW_a , releases from storage under a unit decline in hydraulic head, dh ; $\mathbf{k}$ is the hydraulic conductivity [LT^{-1}]. Hydraulic heads provide a measure of the total mechanical fluid potential, and Eq. 1.3, formulated on the principle of conservation of fluid volume, conserves fluid mass.

To determine the specific discharge the gradient-based Darcy law can be written in the more convenient, indicial notation, form which is valid for the general case of groundwater flow in an anisotropic medium

$$q_i = -k_{ij} \frac{\partial h}{\partial x_j}, \quad (1.4a)$$

where q_i are the components of specific discharge [LT^{-1}], h is the hydraulic head [L], k_{ij} ($i = 1, 2, 3, j = 1, 2, 3$) are the components of symmetrical matrix (tensor) of hydraulic conductivity [LT^{-1}]; coefficient k_{ij} is connected with the permeability, K_{ij} , by the relationship $k_{ij} = K_{ij} \rho g / \mu$. Formula (1.4a) implies the assumption that summation over the same indices is carried out. In the general three-dimensional case $\partial/\partial x_j \equiv \nabla = \partial/\partial x + \partial/\partial y + \partial/\partial z$ is the *Cartesian* coordinate system, ∇ is gradient operator ($\equiv \text{grad}$), sometimes referred to as *Hamiltonian* operator.

Now dissolved passive species will move with the same velocity as water particles (average water velocity) u_i ($\mathbf{u}$)

$$\left. \frac{\partial x_i}{\partial t} \right|_C = u_i = \frac{q_i}{\phi}, \text{ or } \left. \frac{\partial \mathbf{x}}{\partial t} \right|_C = \mathbf{u} = \frac{\mathbf{q}}{\phi}. \quad (1.5)$$

Equation (1.5) specify relationship between the specific discharge, which is used to determine the volumes of fluid passing through given surfaces, and the *actual (advective) fluid velocity* controlling the front of solute movement in the porous space. Actual fluid velocity varies over the pore space, due to the connectivity and geometric complexity of that space. This variable velocity can be characterized by its mean or average value. The average fluid velocity depends on what part of the cross-section area is made up of pores, and to what extent the pore space is connected. Therefore ϕ is the *effective porosity* (*fracture porosity* in fractured rocks) also called kinematic, advective and open porosity.

Taking C as the volumetric concentration of a chemical component (ML^{-3} , M is the amount of the species), the advective flux ($ML^{-2}T^{-1}$) can be expressed in terms of specific discharge (q_i):

$$J_i^a = q_i C = \phi u_i C, \text{ or } \mathbf{J}^a = \mathbf{q} C = \phi \mathbf{u} C. \quad (1.6)$$

Here, J_i^a ($\mathbf{J}^a$) is the mass of a component carried across a unit area, oriented normal to i direction, per unit time. Direction $C\mathbf{q}$ coincides with the direction of fluid motion.

In the cases where solute transport causes the appearance of density gradients or where such gradients originally exist in groundwater systems, the use of hydraulic head as only dependent variable in the analysis neglecting buoyancy component of the flow-driving force is not acceptable (Bachu and Michael 2002; Post et al. 2007). Darcy's specific discharge in such systems should be expressed in terms of a pressure function with allowance made for the space and time variations in the physical characteristics ρ and μ (1.2). Thus, a fluid pressure-based formulation is generally preferable in modeling variable density problems. Such problems, which belong to the class of coupled problems, are considered in the following parts of this book (Chaps. 12–18). The coupling of flow and transport phenomena is caused by the dependence of the water density on the salt concentration.

Strictly speaking, the use of relationship (1.5) implies that the scales and dimensions of the flow and solute migration problems are consistent. Thus, the effective value of the hydraulic conductivity, derived from pumping tests of heterogeneous aquifers, reflects the three-dimensional flow conditions. This value is always greater than the hydraulic conductivity, which governs the migration of components under constrained conditions of a one-dimensional or two-dimensional groundwater flow (Rovey and Niemann 2005). This fact follows from the analysis of basic stochastic models (Gelhar 1993; Neuman 1994), demonstrating the effect of the groundwater flow dimensions on the effective hydraulic conductivity. The ratio of calculated to actual migration velocity values can be as large as two or three, meaning that the rate of aquifer pollution will be considerably overestimated.

1.1.1.2 Effective Porosity (Fracture Porosity)

The characteristic values of active porosity for loose (not cemented, sandy) sediments commonly varies within a relatively narrow range ($\phi \approx 0.2 - 0.4$). In sand type of sediments that have not experienced cementation, the value of ϕ is commonly near the total porosity value ϕ^0 . Silt, loam and clay types of sediments also feature sufficiently high ϕ values ($\phi \approx 0.3 - 0.45$). However, in argillite-like clays, where molecular diffusion dominates, a considerable portion of voids ($\phi^0 - \phi$) is inaccessible for dissolved species (Sect. 1.1.2.1). This is due to the presence of cement “walls” in the pore space. The confirmation is the radical difference between molecular diffusion coefficients obtained in experiments with undisturbed rock samples and with packing clay prepared from the same samples (García-Gutiérrez et al. 2006). Moreover, the diffusion-accessible porosity depends on the type of the migrating ion (Huysmans and Dassargues 2006).

In fractured crystalline rocks and hard sedimentary rocks such as sandstone, limestone and chalk, conceptualized as nonuniform continua with bulk properties, the scatter of parameter ϕ is much wider, while its absolute values are much less

(the average interval is 0.005–0.03). Whence, it follows that the macroscopic transport in fractured rocks, all other conditions being the same, should be much faster than in porous ones.

Clearly, the errors in advection velocity estimates in porous sedimentary deposits are primarily determined by errors in the description of permeability field and the structure of groundwater flows. Variations in the porosity, ϕ , are less significant than the space variations in sediment permeability (hydraulic conductivity), so expert estimates of porosity can be used in some cases, while the hydraulic conductivity no doubt requires detailed experimental studies. Conversely, as it can be seen later, the values of ϕ in fractured type of rock formations are hardly predictable at the intuitive level. Therefore, we have to accept the fact that the results of predicting groundwater pollution in fractured rock complexes, because of their heterogeneity and anisotropism in terms of permeability and advective porosity, are often unreliable.

1.1.1.3 Anisotropy of Sediment and Rock Properties

The form of Darcy's law (1.4a) corresponds to the general case of fluid flow in an anisotropic medium. The hydraulic anisotropy of a bed is the governing factor in the advection in heavily deformed groundwater flow that form, for example, due to concentrated water withdrawal or when density advection develops in the aquifer. Of major importance in sedimentary (porous type) complexes is the anisotropy of permeability in the profile, which is due to the lithologic and facies variability. The anisotropy in fractured-rock complexes is mostly due to the presence of several systems of subvertical fractures (planar anisotropy) and the existence of bedding joints (profile anisotropy). Large tectonic fractures with distinct unidirectional orientation in a medium with primary lithogenetic jointing are most often responsible for planar anisotropy. Therefore, one of the principal anisotropy directions commonly lies in the plane of the water-bearing bed (aquifer), while the other is perpendicular to it.

1.1.1.4 On the Microstructure of Flows in Porous and Fractured Rocks

Active porosity, ϕ , for *unconsolidated or weakly consolidated* (sand–clay) *sediments* is a conventional characteristic, since, in addition to flow-through (active) zones, there always exist stagnant zones not involved in the flow but still playing a considerable role in the formation of the general mass flow (Coats and Smith 1964; van Genuchten and Wierenga 1976; Rose 1977; Golubev 1981): by accumulating the dissolved species via molecular diffusion, such dead-end zones enhance the overall “salt-related” capacity of the system as compared to the active porosity. Therefore, more appropriate characteristic for long-term forecasts would be the value of the total “connected” porosity of rocks (ϕ^0).

Taking into account the interaction between individual elements of flow-bearing media is of fundamental importance for *fractured rocks* (Tsang et al. 1991; Gelhar 1993; Berkowitz 2002; Park et al. 2003; Kosakowski 2004;

Pozdniakov and Tsang 2004). The heterogeneity of the fracture void space is due to tectonic movements, weathering processes, secondary mineral formation, fractures' filling by fine material delivered by infiltration waters from the surface, and karst processes. The major (up to 70–90%) discharge of a fluid moving in such rocks can be concentrated in essentially disjunct channels, which account for as little as 5–20% of the total number of fractures (Rasmuson and Neretnieks 1986; Dahan et al. 1999; Salve 2005). Based on this statistics one may suggest the flow system follows the Pareto's power law related to the class of heavy-tailed distributions. The flow-focusing in individual fractures phenomenon, especially when fractures are intersected by short screens of water extraction/injection wells, can be attributed to their poor hydraulic interaction, which is often the case in the practice, even in heavily fractured rock formations (Berkowitz 2002).

In accordance with the current theoretical views, a continuous (“connected”) flow through a fracture system can form only when the density of fractures with specified geometric characteristics and statistical distribution exceeds some threshold referred to as *percolation threshold*. In the case of idealized model fracture systems with isometric configuration, the critical percolation criteria can be derived analytically or by numerically modeling the flow processes.

For example, in the case of fractures with a length L [L], randomly oriented in a two-dimensional space, theoretical analysis (Pozdniakov and Tsang 2004) yields the following percolation criterion

$$N_2 L^2 \geq \varphi_{2D} = \frac{8}{\pi(1 + 2\varepsilon + \varepsilon^2)}, \quad (1.7)$$

which controls the onset of the flow via interacting fractures; here N_2 is fracture density (the number of fractures per unit area) [L^{-2}], ε is the ratio of the fracture width (in horizontal plane) to its length [LL^{-1}]. This relationship was obtained by the self-consistence method for a system with binary distribution of permeability and is valid for the conditions where the permeability of the matrix (the rock mass between fractures) can be neglected, and the fracture-related porosity of the system $\phi \ll 1$. Thus, the percolation threshold for long thin fractures ($\varepsilon \ll 1$) is $\varphi_{2D} \approx 8/\pi = 2.55$. In the case of three-dimensional groundwater flow in idealized model system represented by fractures in the form of discs, which have diameter D and also are randomly distributed in the space (Pozdniakov and Tsang 2004), the criterion becomes:

$$N_3 D^3 \geq \varphi_{3D} = \frac{9}{4}, \quad (1.7a)$$

where N_3 is the volumetric density of fractures (the number of fractures per unit volume) [L^{-3}].

One should generally expect three-dimensional systems to yield less strict percolation criteria since the probability for fractures to intersect in a three-dimensional space is larger than in a two-dimensional one (Gelhar 1993). In such case, the

existence of individual fractures with anomalously large aperture in a statistically averaged system is not a governing factor in terms of their influence on the effective permeability of the medium: fracture intersections may sometimes exert a greater influence on the overall hydraulic conductivity than do the fracture planes (Neuman 2005).

For qualitative estimates, one can assume that a connected groundwater flow is very likely to form in a fractured rock when each fracture is crossed on the average by 3–5 other fractures. However, when met, such criteria by no means imply that the flow is perfectly similar to a flow in a continuous porous medium, where an overwhelmingly major part of the water-filled space is involved in the formation of flow.

The main factors determining the *channel-type* flow mechanism are high variations in the permeability (hydraulic conductivity) of fractures and poor hydraulic interaction between them. Channeling in the fracture system has an influence on matrix-diffusion mechanisms (Chaps. 6 and 7) because it tends to reduce the effective contact surface between the solute and the matrix (Moreno et al. 1988; Bodin et al. 2003). Thus, this mechanism reduces the damping effect of the porous matrix space (Kurtzman et al. 2005), as well as the role of sorption on fracture surface by reducing the travel times of pollutants (tracers) and increasing the “peak” concentration values, primarily, in processes at relatively small scales. Moreover, when the number of intersections of fractures and channels is small, individual flows through them do not reach complete mixing, as is tacitly recognized by all models (Kupper et al. 1995). This circumstance is one more factor that limits the use of models of equivalent porous media for the description of water and solute transfer in fractured systems.

This implies the need to significantly shift (toward greater values) the customary estimates of elementary representative volume that are based on characteristic distances between fractures: for the continuity condition to be met for a medium, the water-bearing channels in the identified volume should be intersected by a large number of transverse fractures, which ensure the hydraulic interaction between the channels. The channel-based transport mechanism should be taken into account primarily when estimation is made of a situation in the immediate vicinity of a pollution source, as well as when indicator tests of beds are carried out.

Overall, when describing flows in porous media, one often faces situations with high uncertainty, resulting from the lack of reliable information about the location, orientation, length, width, hydraulic interaction, and density of individual fractures and their systems. The uncertainty in forecasts of flow and solute transport in fracture systems has always been considerable (Schwartz et al. 1983; Nordqvist et al. 1996; Tsang et al. 1996; Masciopinto 2005; Neuman 2005).

Having in mind the restrictions that can be imposed on the description of water flow and solute transfer in fractured rocks, let us consider averaged models with bulk rock properties whose development supposes that the medium is continuous within elementary representative volume.

1.1.1.5 Continuity Equations

In the overwhelming majority of practically significant situations, the progress in solute transfer is much slower than the propagation of hydrodynamic perturbations; therefore, Eq. 1.3 can be taken in the steady-state formulation, assuming $\partial h/\partial t = 0$.¹ Now the system of equations describing advection in aquifers, in particular, the advection-induced shift of interfaces between liquids (solutions) with identical physical properties with no regard to diffusion–dispersion phenomena in their contact zone can be written in the following generalized form:

$$\phi \frac{\partial C}{\partial t} + \nabla \cdot (C \mathbf{q}) + W_s = 0, \quad (1.8)$$

$$\nabla \cdot \mathbf{q} + W_f = 0, \quad (1.9)$$

where C is the volumetric concentration of a component in the flowing solution [ML^{-3}]; W_s is the rate at which the mass of the component is produced or disappears per unit volume of the system [$\text{ML}^{-3}\text{T}^{-1}$], e.g., mass-exchange rate between layers with different permeability in stratified systems or fractures and porous matrix in fractured-porous groundwater reservoirs (Chaps. 5 and 6); W_f is the rate at which volume of the fluid is produced or disappears per unit volume of the system [T^{-1}], e.g., areal recharge, interlayer leakage (Chaps. 3–5 and 9).

Equations (1.8) and (1.9) represent a differential form of the mass conservation law for the dissolved substance and flowing fluid. Equation 1.8 is the continuity equation for the mass flux. Its solution describes the concentration distribution forming under the effect of advection in the given domain under given boundary conditions for the solute migration problem. The continuity equation for water flow (1.9) allows one to describe the head field and evaluate the specific discharges as required for solving the former problem.

These equations admit additional transformations. Thus, the well-known formula of vector algebra $\nabla \cdot (C \mathbf{q}) = \mathbf{q} \cdot \nabla C + C \nabla \cdot \mathbf{q}$ allows the system of Eqs. 1.8, 1.9 to be written as

$$\phi \frac{\partial C}{\partial t} + \mathbf{q} \cdot \nabla C + C \nabla \cdot \mathbf{q} + W_s = 0, \quad (1.10)$$

$$\nabla \cdot \mathbf{q} + W_f = 0, \quad (1.11)$$

where $\nabla \cdot \mathbf{q} = \text{div } \mathbf{q} = \partial q_x/\partial x + \partial q_y/\partial y + \partial q_z/\partial z$ is the divergence of the vector field $\mathbf{q}$ (the scalar product of two vectors, ∇ and $\mathbf{q}$).

¹ However, there exists a class of problems where the unsteady-state phase of the flow process may determine behavior of the concentration function (Chap. 9).

Substituting (1.11) into (1.10) yields the following generalized equation

$$\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C - \frac{W_f}{\phi} C + \frac{W_s}{\phi} = 0. \quad (1.12)$$

Such formalization of the process, which preserves the linear form of the transport equation, is possible only in the case where solute transport has no effect on the structure of the flow field.

1.1.2 Molecular Diffusion and Hydrodynamic Dispersion (Microdispersion)

Strictly speaking, the abrupt concentration fronts, as predicted by the model of advection transport, are nonexistent in nature: molecular diffusion and hydrodynamic dispersion result in the formation of a transient (mixing) zone between two liquids, which were initially separated by an abrupt interface.

1.1.2.1 Molecular-Diffusion Transport

The significance of this process increases when the specific discharge is low, primarily, in the flow through low-permeability formations (separation layers, porous blocks of fractured rocks).

Diffusion is a process induced by the random Brownian (thermal) motion of molecules and ions. The diffusive flux through a unit cross-sectional area of a porous *isotropic* medium can be described by *Fick's first law*:

$$J^m = -D_e \nabla C = -\phi D_m \nabla C, \quad (1.13)$$

where J^m is the diffusion flux [$\text{ML}^{-2}\text{T}^{-1}$], C is the concentration [ML^{-3}], D_e and $D_m = D_e/\phi$ are the *effective diffusion* and *pore diffusion coefficients* [L^2T^{-1}] (Ruthven 1984). D_e is a coefficient characterizing steady-state diffusion flux. Coefficient D_m describes transient diffusion and is a parameter included in the Fick's second law (see Sect. 1.1.2.5). Along with D_e and D_m , an *apparent diffusion coefficient*, D_a , can be used to characterize migration of sorbed species. It takes into account not only the geometry of the porous medium but also the retardation factor, R (Sect. 1.5.1): $D_a = D_m/R$.

Thus, the relationship between the different dispersion coefficients is therefore:

$$D_m = D_a R = D_e / \phi. \quad (1.13a)$$

The driving force for the one-dimensional (along the x direction) diffusion is the quantity $-\partial C / \partial x$, thus in a simple one-dimensional system at uniform temperature and pressure under steady state conditions

$$J_x^m = -D_e \frac{dC}{dx}. \quad (1.14)$$

Results of laboratory and field tests show that the diffusion coefficient depends on the magnitude of the porosity and on its spatial distribution. The basic equation is:

$$D_e = D^0 \phi \tau, \quad (1.15)$$

where D^0 is the diffusion coefficient in bulk water [L^2T^{-1}], ϕ is the *diffusion-accessible porosity* [L^3L^{-3}], τ is the *tortuosity* [L^2L^{-2}] which accounts for the pore geometry (Grathwohl 1998) and ranges between 0.01 and 0.5 for most geological materials.

An alternative presentation for D_e follows from the formal analogy between diffusion and electrical conductivity in porous sediments (Boving and Grathwohl 2001):

$$D_e = D^0 \phi^m \quad (1.16)$$

(Archie's law), where m is an empirical exponent (cementation or shape factor). The value of m lies between 1.3 and 5.4 (Polak et al. 2002), depending upon rock consolidation and some other factors. Studies focused on different limestone and sandstone rocks, argillaceous rocks and chalk showed that the data for various inorganic and organic compounds resulted in an exponent between 1.5 and 2.5 (Boving and Grathwohl 2001; Polak et al. 2002; van Loon et al. 2003; Blum et al. 2007). It is very likely that $m = 2$ corresponds to the upper limit for a rock matrix with porosity < 0.2 (Liu et al. 2004). At least this value may be taken for preliminary expert assessments for the mentioned rock types.

The values of coefficient D_e in porous water-bearing rocks are several times less than the molecular diffusion coefficient D^0 in a free solution, where $D^0 = (1 - 2) \cdot 10^{-9} \text{ m}^2/\text{s}$ for most electrolyte ions. The values of D_e determined experimentally for weakly lithified sand-clay sediments (with the use of tracers, such as Cl^- , NO_3^- and ^3H) commonly vary within $(1-5) \cdot 10^{-10} \text{ m}^2/\text{s}$. The diffusion coefficients in sandy sediments are always higher than the diffusion in clay-silt-type sediments of the same porosity.

In the general case, coefficient D_e is strongly dependent on the size of molecules of the diffusing solute and its ionization degree. Also it has been reported in many publications that the effective diffusion coefficient for cationic-species through clay systems is systematically higher than the value for HTO (isotope ^3H). This enhanced diffusion for cations is generally referred to as "surface diffusion" (Maes et al. 2008).

When a species migrates in stratified (layered) beds (Chap. 5), represented by elements with different permeability (clay bands and lenses in sand deposits), the molecular diffusion acts as a factor that levels the concentrations by redistributing the solute from elements with higher permeability (responsible for the majority of advection transport) to elements with lower permeability. Thus it contributes to the formation of a transitional zone with gradually changing concentration at the front separating the replacing and being replaced solutions and reduces the rate of front motion.

Molecular diffusion coefficient is a key parameter governing solute transport in fractured-porous media (Chap. 6). A vast body of experimental data is available, characterizing the diffusion of components in the *porous matrix* of fractured rocks of different genetic types. Depending on the genesis and the degree of lithification (or metamorphization) of rocks, parameter D_e varies within a wide range – from $n \cdot 10^{-10}$ to $n \cdot 10^{-15}$ m²/s. This parameter attains its maximal values (up to $5 \cdot 10^{-10}$ m²/s) in chalk-marl deposits with block porosity, ϕ_m of 35–40% (Mironenko and Rumynin 1986; Zuber and Motyka 1994; Little et al. 1996; Polak et al. 2002; Mathias 2005; Mathias et al. 2005). Porous blocks of sandstones and limestones ($\phi_m = 10$ –15%) feature the values of 10^{-10} – 10^{-11} m²/s. Experiments with tufaceous formations ($\phi_m = 6$ –37%) yielded the values $D_e = (0.2$ – $2) \cdot 10^{-11}$ m²/s (Reimus et al. 2007). The values of D_e obtained in experiments with tufaceous formations ($\phi_m = 0.2$ –2%) were of the order of 10^{-13} m²/s (Rumynin et al. 1998). Many fractured “hard rocks” (with practically impermeable blocks) contain a well-developed system of voids available for molecular diffusion of species, especially near the fracture surfaces; here the values of D_e are of the order of 10^{-12} – 10^{-14} m²/s (Reimus et al. 2003).

Especially thorough recent studies in many countries have been focused on the diffusion properties of regionally persisting clay formations with a large (>100 m) thickness, which are of interest in the context of their possible use for long-term isolation of radioactive wastes (RW). Molecular diffusion is regarded as the main radionuclide transport mechanism in the estimation of the risk associated with RW burial. Thus, a number of lab and in situ tests has been performed to study diffusion in Aalenian Opalinus clay (Switzerland), Rupelian Boom clay at Mol (Belgium), Callovo-Oxfordian clayey siltstone/silty clay at Bure (France), Vendian/Kothlin, Cambrian/Blue clays (the north-western region of Russian Federation) (see Chap. 22).

The studies show all these strata to feature *anisotropic diffusion properties*: the effective-diffusion coefficient along the beds, D_{eL} , is many times greater than the same coefficient D_{eT} governing the solute transfer across the beds (Palut et al. 2003; Yllera et al. 2004; Clay Club Catalogue... 2005; García-Gutiérrez et al. 2006; Samper et al. 2006; Samper et al. 2008; Soler et al. 2008; Cormenzana et al. 2008; Rumynin et al. 2009; see also Sects. 22.7.2 and 22.7.3 in this book). This difference is due to the microstratification of clay strata, i.e., alternation of beds (with thickness varying from several millimeters to a few centimeters) with different concentrations of clay minerals. Such effect can be caused, for example, by intercalation of argillite and aleurolite. The anisotropy of the effective diffusion coefficient is due to stratification, the preferred orientation of the microlayers at the mm-cm scale. The tortuosity of the diffusion pathways is larger when the direction is normal rather than parallel to the preferred orientation of the layers (Suzuki et al. 2004). So, diffusion anisotropy is a consequence of rock heterogeneity and bedding.

Tracer transport in an anisotropic clay domain is described by the following diffusion equation (Bear 1972; Crank 1975; Palut et al. 2003; Samper et al. 2006, 2008; Soler et al. 2008):

$$\frac{\partial C}{\partial t} - \nabla \cdot (\mathbf{D}_m \cdot \nabla C) = 0, \quad (1.17)$$

where $\mathbf{D}_m$ is the orthotropic pore diffusion tensor. The expression for the latter is as follows:

$$\mathbf{D}_m = \begin{pmatrix} D_{mL} & 0 & 0 \\ 0 & D_{mL} & 0 \\ 0 & 0 & D_{mT} \end{pmatrix}, \quad (1.18)$$

where D_{mL} and D_{mT} are the principal components of the tensor. In this study, D_{mL} is the effective pore diffusion coefficient parallel to the *horizontal* bedding while D_{mT} is the effective pore diffusion coefficient perpendicular to the bedding.

The values of the molecular diffusion coefficient commonly correlate only slightly with aquifer material permeability, though there are some exceptions (Boving and Grathwohl 2001; Reimus et al. 2007). Some researchers found laboratory estimates of D_e to be less than the values determined in the field (Zhou et al. 2007). Such difference is primarily due to the existence of a weathering (degradation) zone at the contact between a porous block and a fracture, as well as the presence of stagnant water in dead-end microfractures.

1.1.2.2 Mechanical Dispersion (Hydrodynamic Dispersion) of Solutes

This phenomenon is due to two effects: (1) a dynamic effect, i.e., local (at the pore scale) variability of flow velocity field; and (2) kinematic, i.e., the branching of trajectories of motion in the pore space. Their combination looks like a diffusion process, facilitating the formation of a transient (in terms of concentration) zone between the solutions replacing and being replaced.

Hydrodynamic dispersion can be considered jointly with molecular diffusion, and is in many cases taken to be a *Fickian process*, whose transport law takes the form of *Fick's law* of molecular diffusion (1.13)

$$\mathbf{J}^d = -\phi \mathbf{D} \nabla C, \quad (1.19)$$

where $\mathbf{J}^d$ is the vector of total dispersion flux [$\text{ML}^{-2}\text{T}^{-1}$], C is the concentration [ML^{-3}], $\mathbf{D}$ is the total dispersion coefficient (second order tensor) [L^2T^{-1}]. The dispersion flux (1.19) can be presented in the indicial notation form

$$J_i^d = -\phi D_{ij} \frac{\partial C}{\partial x_j}. \quad (1.19a)$$

Similar to hydraulic conductivity, k_{ij} , in the Darcy's law (1.4a), equality (1.19a) for Fickian dispersion is valid for the general case of an anisotropic porous medium.

Despite the mathematical similarity of the two fundamental laws, (1.4a) and (1.19a), there is a basic difference between the coefficients k_{ij} and D_{ij} (Bear and Cheng 2010): the former is a function of the microscopic geometry of the void space, while the latter depends also on the macroscopic velocity field. The properties of the dispersion coefficient for isotropic and anisotropic models of porous media are thoroughly investigated by Bear and Cheng (2010).

In the general case of isotropic porous medium, this total dispersion coefficient depends on the specific discharge and comprises a hydrodynamic, D_{ij}^h , and a molecular-diffusion, D_m , components (Bear 1972):

$$D_{ij} = D_{ij}^h + D_m \delta_{ij}, \quad (1.20)$$

$$D_{ij}^h = \left[(\delta_L - \delta_T) \frac{u_i u_j}{|u|^2} + \delta_T \delta_{ij} \right] |u|, \delta_{ij} \begin{cases} = 1 & \text{for } i = j, \\ = 0 & \text{for } i \neq j, \end{cases} \quad (1.21)$$

where δ_L and δ_T are the longitudinal and transverse *dispersivity* of the porous medium (factors in the linear relationship between components of hydrodynamic dispersion D_{ij}^h and fluid actual velocity u_i/u_j) [L], D_m is the pore diffusion coefficient [$L^2 T^{-1}$], $|u| = u = (u_x^2 + u_y^2 + u_z^2)^{1/2}$, δ_{ij} is *Kronecker's delta function* [–], $i, j = 1, 2, 3$.

For example, in a unidirectional (along the x axis) horizontal flow:

$$D_{xx} \equiv D_L = \delta_L u_x + D_m, \quad D_{yy} = D_{zz} \equiv D_T = \delta_T u_x + D_m. \quad (1.22)$$

The *longitudinal dispersivity*, δ_L , reflects the variability of pores and fractures geometry. This proportionality constant is accepted to be a characteristic length scale of the medium. Having been measured for a relatively identical spatial scale, dispersivity of fractured rocks usually exceeds dispersivity of granular type of formations. Dispersivity values measured at typical interwell distances (100–1,000 m) are about two to four orders of magnitude larger than those measured in the lab (0.1–1 m).

The systematization and generalization of the vast body of experimental material is a focus of numerous publications (Facets of hydrology 1976; Pickens and Grisak 1981; Alexeev et al. 1989; Neuman 1990; Gelhar et al. 1992; Gelhar 1993; Schulze-Makuch 2005). Collected dispersivity data demonstrate that laboratory experiments lead to longitudinal dispersivity values in the range 10^{-4} – 10^{-2} m whereas they fall in the range 10^{-2} –1 m for field tracer experiments and cover a range of 1 to $N10$ – $N100$ m for modeling of long-term behavior of global tracers and industrial waste in aquifers. These differences are commonly attributed to heterogeneities (aquifer stratification or/and dual porosity) inherent at the field scale (Woumeni and Vauclin 2006).

Therefore the use of the linear dependence $D_L(u)$, Eq. 1.21, with proportionality constant, δ_L , for the description of mechanical dispersion of solute in heterogeneous media is not justified. Longitudinal dispersivity values measured over a range of length scales have been shown to grow with distance. The scaling relationship of longitudinal dispersivity, δ_L , with scale of measurement, L , below an upper bound can be described by the empirical power law (Schulze-Makuch 2005): $\delta_L = c(L)^m$, where c is a parameter-characteristic for a geological medium, m is a scaling exponent. Field data analysis showed that the scaling exponent for all geological media is in the range between 0.40 and 0.94.

The upper bound represents the volume at which a porous medium becomes the equivalent of a homogeneous medium, and thus the dispersion is of classical Fickian character, i.e. above the upper bound longitudinal dispersivity remains constant with scale. Such asymptotic behavior of the relationship (1.21) attains only when the

scale of the transport process analysis is at least an order of magnitude greater than the velocity correlation scale or characteristic size of the heterogeneity elements. However, under real field condition the necessary upper bound for solute transport may be never attained. For example, such situation may occur in large-block fracture rocks and in media with channel-type mechanism of flow/solute transfer.

Transverse hydrodynamic dispersion, resulting in solute redistribution across the flow direction, causes the formation of two- or three-dimensional dispersion plumes. Its constant δ_T is commonly assumed to be 10–20 times less than the value of δ_L , though this is more or less true only for homogeneous media, while δ_T/δ_L ratios in heterogeneous media are strongly dependent on flow configuration (Rehfeldt and Gelhar 1992).

Overall, the transverse dispersion (along with molecular diffusion and fluctuations of velocity fields over time) is the key factor of solute spreading, whose role *increases* (as opposed to longitudinal dispersion) with increasing scale of transfer, more precisely, the lateral surface areas of the migrating plume. A result of such spreading is some *retardation* of the longitudinal solute transfer and leveling of concentration distribution within an aquifer system.

In some studies based on the analysis of field material, the dispersion properties of water-bearing strata in the directions orthogonal to the direction of advection were found to be anisotropic: the difference between the values of δ_{T_H} and δ_{T_V} , which characterize the hydrodynamic dispersion in the horizontal and vertical directions, can be as large as two orders of magnitude (commonly, $\delta_{T_H} > \delta_{T_V}$), which is most likely due to the natural stratification of geological media. As was the case with longitudinal dispersion, the heterogeneity of the medium also results in the values of δ_T being noninvariant and dependent on the scale at which the process is being analyzed.

Thus, in transversely isotropic porous medium with horizontal stratification the dispersion tensor shall be defined by three dispersivities: a longitudinal dispersivity, δ_L , and two transversal dispersivities, a horizontal one, δ_{T_H} , and a vertical one, δ_{T_V} . The components of the dispersion tensor in three dimensions are presented (Bear and Cheng 2010) as

$$D_{xx}^h = \frac{1}{u} (\delta_L u_x^2 + \delta_{T_H} u_y^2 + \delta_{T_V} u_z^2), \quad (1.23a)$$

$$D_{yy}^h = \frac{1}{u} (\delta_{T_H} u_x^2 + \delta_L u_y^2 + \delta_{T_V} u_z^2), \quad (1.23b)$$

$$D_{zz}^h = \frac{1}{u} (\delta_{T_V} u_x^2 + \delta_{T_V} u_y^2 + \delta_L u_z^2), \quad (1.23c)$$

$$D_{xy}^h = D_{yx}^h = \frac{1}{u} (\delta_L - \delta_{T_H}) u_x u_y, \quad (1.23d)$$

$$D_{xz}^h = D_{zx}^h = \frac{1}{u} (\delta_L - \delta_{T_V}) u_x u_z, \quad (1.23e)$$

$$D_{yz}^h = D_{zy}^h = \frac{1}{u} (\delta_L - \delta_{T_V}) u_y u_z. \quad (1.23f)$$

In this study we will mostly analyze the situations that correspond to sufficiently large transfer scales, which allows the use of linear model (1.20) with constant parameters δ_L and δ_T .

1.1.2.3 On the Contributions of Individual Mechanisms Responsible for Solute Spreading in Porous Media

The summands in formulas (1.20) and (1.22) reflect the rate of molecular-diffusion and mechanic-dispersion mass transfer in a liquid flow. The role of each factor in the overall balance of mass flux is governed, other conditions being the same, by the specific discharge and aquifer sediment structure. Analysis of experimental material (Rose 1977; Batu 2006) allows several characteristic solute transfer regimes to be identified, reflecting the significance of molecular diffusion and mechanical dispersion: molecular diffusion completely determines the dispersion transfer when $0 \leq \xi = qd_e/D^0 < 0.1$ (here d_e is the effective diameter of sediment matrix grains, D^0 is molecular diffusion coefficient in a free solution); when $0.1 \leq \xi < 5$, the contribution of molecular-diffusion and mechanical-dispersion components to the smoothing of concentration fronts is about the same; and finally, $\xi > 5 - 10$ is the domain of predominance of mechanical dispersion in the general longitudinal dispersion of solute. These intervals shift in the case of transverse dispersion: molecular dispersion, as it was mentioned above, contributes notably to the formation of dispersion plumes even when the specific discharge is relatively large.

1.1.2.4 On Hydrodynamic Dispersion in Fractured Rocks

The behavior of dispersion plumes in such media is strongly dependent on the density of fractures, the statistical distribution of their length and permeability, and the presence in the rock formation of several fracture systems with different spatial orientation. The combination of governing characteristics can be such that the description of concentration distribution based on classical dispersion concepts (models) would be inadequate. The concentration distribution often differs from that predicted by classical dispersion models when there are *dominating* systems of long fractures in the rock formation (Reeves et al. 2008b). The distribution of groundwater flows between such systems and small fractures is very complicated, even with the formation of local circulation cells, which have little effect on the general (averaged) groundwater flow, but change the character of concentration curves (Park et al. 2003; Kosakowski 2004). Such effects stimulate the development of alternative models of flow and solute transport in *discrete* fractured space. Models of this type are of particular importance in the context of predicting long-term consequences of isolation of radioactive wastes in hard-rock formations at large depths. In the upper part of the geological section, when the density of weathering joints is large enough, the application of averaged dispersion models is less problematic.

1.1.2.5 Continuity Equation

The general form of advection–dispersion equation results directly from the continuity equation:

$$\phi \frac{\partial C}{\partial t} = -\nabla \cdot (\mathbf{J}^a + \mathbf{J}^d) - W_s = 0, \quad (1.24)$$

where $\mathbf{J}^a$ and $\mathbf{J}^d$ are advective (1.6) and dispersive (1.19) fluxes. Considering this equation together with flow Eq. 1.9 one can obtain

$$\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C - \nabla \cdot (\mathbf{D} \cdot \nabla C) - \frac{W_f}{\phi} C + \frac{W_s}{\phi} = 0, \quad (1.25)$$

where $\mathbf{u}$ and $\mathbf{D}$ are groundwater velocity (real fluid velocity) and coefficient of total dispersion. For the case of no flow regime ($q = 0$) Eq. 1.25 becomes formally similar to the unsteady state diffusion equation (the *second Fick's law*).

A sink/source term W_s in Eq. 1.24 can be used in order to expend the advection–dispersion model to include nonequilibrium transfer between mobile and immobile regions or between liquid and solid phases for describing solute transport in physically or chemically heterogeneous porous medium (Chaps. 6–8, 20). W_f is normally areal ground water recharge (Chaps. 3 and 4) or vertical leakage term in stratified systems (Chap. 9).

1.1.3 Initial and Boundary Conditions; Definitions of Concentration Functions

To obtain closed-form solutions for solute and flow balance equations, one needs to provide a mathematical formulation of initial and boundary conditions.

The *initial condition* for solute transport problems is commonly presented in the form of homogeneous concentration distribution throughout the domain

$$C(x, y, z, 0) = C^0. \quad (1.26)$$

The *boundary conditions* are formulated as:

- first-type boundary condition or *Dirichlet* condition

$$C = C_0(x, y, z, t), \quad (1.27)$$

where $C_0(x, y, z, t)$ is a concentration function specified on domain boundaries, in particular, $C_0 = \text{const}$ (a step input of solute at a concentration of C_0);

- second-type boundary condition or *Neumann* condition

$$\left(\phi D_{ij} \frac{\partial C}{\partial x_j} \right) n_i = Q_c(x, y, z, t), \quad (1.28)$$

where n_i are components of a unit vector normal to the boundary, $Q_c(x, y, z, t)$ is the specified specific dispersion flux of the solute (zero flux $Q_c = 0$ on one or several boundaries of the domain is an example);

- third-type boundary condition or *Cauchy* condition

$$\left(\phi D_{ij} \frac{\partial C}{\partial x_j} - q_i C \right) n_i = Q_c(x, y, z, t), \quad (1.29)$$

where the first and second terms in parentheses in the left part of the equation account for the dispersion and advection fluxes on the domain boundary, respectively.

As a counter to the point (*resident*) concentration C_R (C in the former denotations), which is determined by the solute content of a macroscopic (elementary) volume of the pore medium, i.e., is a static characteristic, *flux* concentration C_F is a more adequate means to characterize solute transport in the models being constructed (Kreft and Zuber 1978; Batu 2006; Cornaton and Perrochet 2006; Govindaraju and Das 2007). Concentration C_F accounts for the mass of solute M , which passes through a cross-section of a streamtube under the effect of advection and dispersion transport, i.e., it is a dynamic characteristic. Essentially, the flux concentration is the ratio of the mass flux of dissolved solutes to the volumetric flux of the liquid (Kreft and Zuber 1979). Let in a one-dimensional case, $M = (qC_R - \phi D_L \frac{\partial C_R}{\partial x}) S dt$ (S is flow cross-section area); now, by definition, $C_F = M/V$, where $V = qSdt$. This yields the relationship between the two types of concentrations in differential form:

$$C_F = C_R - \frac{D_L}{u} \frac{\partial C_R}{\partial x}. \quad (1.30)$$

On the other hand, one may assume (Zhang et al. 2006) that conservation of mass requires that passes through a given control plane at location x through time t must be equal the total mass downstream of x at time t :

$$\phi u \int_0^t C_F(x, t') dt' = \phi^0 \int_x^\infty C_R(x', t) dx'. \quad (1.30a)$$

where ϕ and ϕ^0 are the mobile and total porosities (Sect. 1.1.1.4). If there is no partitioning to immobile water, Eq. 1.30a leads to the following definition for C_F in integral form (Kreft and Zuber 1978):

$$C_F(x, t) = \frac{1}{u} \frac{\partial}{\partial t} \int_x^\infty C_R(x', t) dx'. \quad (1.31)$$

For 3D microdispersion, concentration C_F can be converted into C_R through the integral expression (Batu 2006):

$$C_R(x, y, z, t) = \frac{u}{D_L} \exp\left(\frac{ux}{D_L}\right) \int_0^\infty \exp\left(-\frac{ux'}{D_L}\right) C_F(x', y, z, t) dx'. \quad (1.31a)$$

The relationships presented here are valid for one-dimensional steady-state flows with constant velocity whose vector is perpendicular to the inlet boundary, $x = 0$.

In most lab or field experiments, the observed concentration profiles are obtained by measuring the concentrations in volume of the fluid extracted from porous media, e.g., in the fluid coming out of the exit boundary (Kocabas and Islam 2000). Therefore, the solutions employed in interpretation of experimental and monitoring data must be in terms of flux concentration. Formally, Eqs. 1.30 and 1.31 allow one to derive solutions for function C_F given analytical expressions for function C_R (Batu 2006). However, the contrast between C_F and C_R is perceivable only at low *Peclet numbers* ($Pe = ux/D_L$), tentatively at $Pe < 5$. Thus, the differentiation in the understanding of concentration function for classical Fickian diffusion in homogeneous media is significant for the analysis of the process within a limited range of conditions. However, in heterogeneous or dual-porosity media with anomalous dispersion, or in media having preferential pathways, the resident and flux concentrations may differ appreciably (Kim and Feyen 2000; Zhang et al. 2006).

1.2 Models for Advective Transport in Homogeneous Isotropic Media

The approaches to the analysis of advection in aquifers aimed to reduce the number of independent variables are based on the assumption that the hydrodynamic field is independent of the concentration field. The dimension of the problem could be reduced if we succeed in constructing streamlines or converting linear coordinates x , y and z by a complex potential function related to the specific discharge function and stream function.

1.2.1 A Characteristics-Based Method for Solving the Transport Equations

In the general three-dimensional case, Eq. 1.12, describing transport in a steady-state flow field without sources ($W_f = 0$ and $W_s = 0$), can be reduced to

$$\frac{\partial C}{\partial t} + u_x \frac{\partial C}{\partial x} + u_y \frac{\partial C}{\partial y} + u_z \frac{\partial C}{\partial z} = 0, \quad (1.32)$$

where u_x , u_y , u_z are principal components of the real flow velocity; each of the components may depend on all three space coordinates.

Equation 1.32 is a first-order linear homogeneous equation in concentration function C with four independent variables. As regards this equation, of greatest interest for us is the solution of the *Cauchy problem*, which can be formulated in two ways for the migration problems in question. The first, unsteady-state formulation

assumes that the concentration profile is specified at the initial time ($t = 0$) and the distribution $C = C(x, y, z, t)$ for any moment, t , is to be found. The second, steady-state formulation assumes that the concentration profile is specified in some initial section and the concentration distribution is to be found in the flow after the initial section (at $t \rightarrow \infty$).

Several approaches to the solution of Eq. 1.32 are available. A convenient and demonstrative method is based on the preliminary solution of auxiliary equations that form an integral basis for the construction of general and particular solutions of the original equation.

Partial differential equation (1.32) is known to be associated with the system of first-order ordinary differential equations:

$$\frac{dt}{1} = \frac{dx}{u_x} = \frac{dy}{u_y} = \frac{dz}{u_z}. \quad (1.32a)$$

Proofs of this property of first-order linear partial differential equations can be found in a series of textbooks and monographs.

System of Eqs. 1.32a is referred to as a characteristic system, and its integral curves are called characteristics. If velocities u_x , u_y and u_z have continuous partial derivatives with respect to all arguments and the condition $u_x^2 + u_y^2 + u_z^2 \neq 0$ is met, then only one characteristic passes through any point in the domain.

System of Eqs. 1.32a can be rewritten as three independent equations:

$$\frac{dx}{dt} = u_x, \quad \frac{dy}{dt} = u_y, \quad \frac{dz}{dt} = u_z. \quad (1.33)$$

Their general solutions yield an integral basis

$$w_1(x, y, z, t) = c_1, \quad w_2(x, y, z, t) = c_2, \quad w_3(x, y, z, t) = c_3 \quad (1.34)$$

for the construction of a general solution of Eq. 1.31 in the form (Polyanin et al. 2002)

$$C = \Phi(w_1, w_2, w_3); \quad (1.35)$$

here Φ is an arbitrary function of three arguments, c_i are integration constants. Equalities (1.34) represent a parametric form of solution to Eq. 1.33. They describe some surfaces in a three-dimensional space. The intersection of these surfaces provides information about the position of a particle in the space at time t . Taken together, they describe the trajectories of particles in the space.

The initial condition for classical Cauchy problem has the form

$$t = 0 \quad C = \varphi(x, y, z), \quad (1.36)$$

where $\varphi(x, y, z)$ is a known function. This condition is conveniently represented in the parametric form (Polyanin et al. 2002):

$$t = 0 \quad x = \xi_1, \quad y = \xi_2, \quad z = \xi_3, \quad C = \varphi(\xi_1, \xi_2, \xi_3). \quad (1.37)$$

The solution of Cauchy problem consists in substituting the initial data (1.37) for independent variables in integral (1.34) for characteristic system (1.32a) and adding the obtained expressions to the latter equality (1.37)

$$\begin{aligned} w_1(0, \xi_1, \xi_2, \xi_3) &= c_1, & w_2(0, \xi_1, \xi_2, \xi_3) &= c_2, \\ w_3(0, \xi_1, \xi_2, \xi_3) &= c_3, & C &= \varphi(\xi_1, \xi_2, \xi_3). \end{aligned} \quad (1.38)$$

Next ξ_1 , ξ_2 and ξ_3 are expressed in terms of c_1, c_2 and c_3 from the first three Eqs. 1.38 and substituted into the right part of the last equality (1.38). The result is the dependence

$$C = \varphi(c_1, c_2, c_3), \quad (1.39)$$

which is the required solution of the problem.

Let us consider as an example the following one-dimensional equation

$$\frac{\partial C}{\partial t} + u_x \frac{\partial C}{\partial x} = 0, \quad (1.40)$$

where $u_x = a + bx$ is an increasing velocity, a is the velocity in section $x = 0$ [LT^{-1}], b is the gradient of the velocity increase [T^{-1}]. We take the initial condition in the form of the linear distribution

$$t = 0 \quad \bar{C} = \varphi(x) = 1 - \gamma x; \quad (1.41)$$

here $\bar{C} = (C - C_2)/(C_1 - C_2)$ is the relative concentration ($0 \leq \bar{C} \leq 1$), C_1 and C_2 are concentrations at the boundary of the transitional zone, γ is a constant [L^{-1}]. Such problem can be associated, for example, with the problem of displacement of a diffused natural contact of salt and fresh groundwater under the effect of water intake through a row of wells.

The partial differential Eq. 1.40 corresponds to the ordinary differential equation

$$\frac{dt}{1} = \frac{dx}{a + bx}, \quad (1.42)$$

which yields the integral basis

$$w_1(x, t) = (a + bx)e^{-bt} = c_1 \quad (1.43)$$

for the general solution (in a dimensionless form)

$$\bar{C} = \Phi(a + bx) e^{-bt}. \quad (1.44)$$

To find the solution of Cauchy problem, let us represent the initial condition (1.41) in the parametric form

$$t = 0 \quad x = \xi \quad \bar{C} = (1 - \gamma \xi). \quad (1.45)$$

Substituting (1.43) at $t = 0$ yields

$$\bar{C} = 1 - \gamma \frac{c_1 - a}{b}. \quad (1.46)$$

After the substitution of c_1 from (1.43) into (1.46), we finally obtain

$$\bar{C} = 1 - \gamma \frac{(a + bx) e^{-bt} - a}{b}. \quad (1.47)$$

This solution can be conveniently presented in another characteristic form:

$$x = f(t, \bar{C}) = \left[\frac{1}{\gamma}(1 - \bar{C}) + \frac{a}{b} \right] e^{bt} - \frac{a}{b}. \quad (1.48)$$

At $b = 0$ (uniform motion), we have

$$x = f(t, \bar{C}) = \frac{1}{\gamma}(1 - \bar{C}) + at. \quad (1.48a)$$

The deviation of characteristic curves from straight lines (e.g., as can be seen from the example of calculation in Fig. 1.1) can be attributed to the different motion velocities of concentration points $\bar{C}$ in the flow whose velocity linearly depends on the x coordinate (Fig. 1.1).

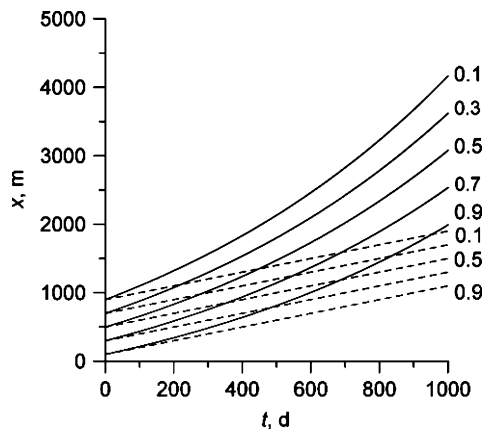
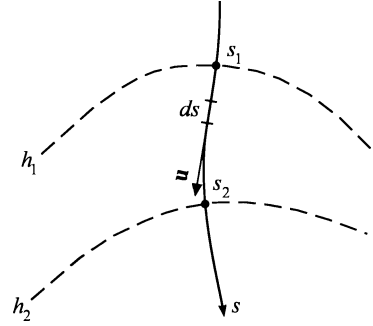


Fig. 1.1 Example of a plot for characteristic curves derived from solution (1.48) at $\gamma = 0.001 \text{ m}^{-1}$, $a = 1.0 \text{ m d}^{-1}$, $b = 0.001 \text{ d}^{-1}$ (full lines) and $b = 0$ (dashed lines)

Fig. 1.2 Illustration for the evaluation of particle travel time along a streamline s (full line) between points s_1 and s_2 ; h_1 and h_2 are hydro-isopiestic lines (dashed lines)



Analysis of solutions of advective-transport equations with the help of the method of characteristics is convenient in studying the mutual superposition of concentration fronts (the trailing and leading edges, in the case of discrete solute-concentration time series input into the bed) when nonlinear sorption processes are involved or when the solutions contain substances that have cross effects on their sorption characteristics (Charbeneau 1981, 1982, 2000).

Given the flow structure, the travel time of any particle of dissolved species along trajectory s (Fig. 1.2) between two points (s_1 and s_2) is the sum of times dt required for the particle to cover elementary segments ds :

$$t_{12} \equiv t_0 = \int_{s_1}^{s_2} \frac{ds}{u(s)}, \quad (1.49)$$

where u is the magnitude of the real flow velocity.

Now the problem's solution in the characteristic form can be written as

$$dC = 0 \text{ along } t - \int_{s_1}^{s_2} \frac{ds}{u(s)} = \text{const.} \quad (1.50)$$

1.2.2 Solute Transport Process Analysis in Curvilinear Coordinates

1.2.2.1 Basic Concepts of Potential-Flow Functions

In the theory of flow in porous medium, it is often advantageous to introduce a function $\varphi(x, y, z)$, referred to as *specific discharge potential* (or potential function) and defined in a confined flow (homogeneous medium) as

$$\varphi = kh, \quad (1.51)$$

where k is the hydraulic conductivity, h is the head.

Now the specific discharge of the flow can be expressed in terms of the gradient of specific discharge potential

$$\mathbf{q} = -\nabla\varphi. \quad (1.52)$$

From the continuity Eq. 1.9 ($W_f = 0$), it follows that function φ satisfies the Laplace equation

$$\nabla^2\varphi = 0, \quad (1.53)$$

where ∇^2 is the Laplacian.

In the two-dimensional horizontal formulation (in the x - y plane), $\varphi = \varphi(x, y)$ and we have

$$q_x = -\frac{\partial\varphi}{\partial x}, \quad q_y = -\frac{\partial\varphi}{\partial y}, \quad (1.54)$$

so the Laplacian becomes

$$\nabla^2\varphi = \frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} = 0. \quad (1.55)$$

Specific discharge components (1.54) can be also expressed in terms of an auxiliary function $\psi = \psi(x, y)$:

$$q_x = \frac{\partial\psi}{\partial y}, \quad q_y = -\frac{\partial\psi}{\partial x}, \quad (1.56)$$

as one can readily see by substituting relationships (1.56) into continuity Eq. 1.9.

Since partial differential Eq. 1.8 ($W_s = 0$) corresponds, as we know (Sect. 1.2.1), to the ordinary differential equation

$$\frac{dx}{q_x} = \frac{dy}{q_y}, \quad (1.57)$$

we can write

$$q_y dx - q_x dy = 0. \quad (1.57a)$$

Substituting relationships (1.56) for specific discharge components into the latter equation yields the total differential of function $\psi(x, y)$:

$$\frac{\partial\psi}{\partial x} dx + \frac{\partial\psi}{\partial y} dy = d\psi = 0, \quad (1.58)$$

whence we have $\psi(x, y) = \text{const}$. Thus, function ψ represents a family of curves derived by equaling function $\psi(x, y)$ to an arbitrary constant. These curves are streamlines, and function $\psi = \psi(x, y)$ is referred to as *stream function*.

If we draw a line between points 1 and 2 in plane x - y , liquid flux Q_{12} through this line will be equal to the difference between stream function values in those points, whatever the shape of the line

$$Q_{12} = \psi_2 - \psi_1. \quad (1.59)$$

To describe a general *three-dimensional* flow, one needs three coordinates. In such case, we can introduce a pair of functions of those coordinates, which will correspond to two families of mutually intersecting *stream surfaces*, whose intersections are streamlines. Thus, the stream function in the case of three-dimensional flow is not scalar, since to determine it one needs to specify the equations of the surfaces.

Analytical expressions for stream functions allow one to determine the shape (structure) of streamlines, which, in the case of steady flow, represent the trajectories of particles of water and dissolved species.

Well-developed methods for the solution of two-dimensional horizontal potential flows in various domains based on the application of complex variable theory can be used to construct two-dimensional functions $\varphi(x, y)$ and $\psi(x, y)$. The basis for such approach is the existence of an analytical relationship between the velocity potential gradient and the stream function

$$\frac{\partial \varphi}{\partial x} = \frac{\partial \psi}{\partial y}, \quad \frac{\partial \varphi}{\partial y} = -\frac{\partial \psi}{\partial x}, \quad (1.60)$$

which follows from Eqs. 1.54 and 1.56. These relationships between the derivatives of functions φ and ψ are the well-known *Cauchy–Riemann equations*.

The behavior of both functions $\varphi(x, y)$ and $\psi(x, y)$ is described by the Laplace equations

$$\nabla^2 \varphi = 0, \quad \nabla^2 \psi = 0, \quad (1.61)$$

whence it follows that an orthogonal function ψ corresponds to any function φ and vice versa.

The properties of linear homogeneous equations of Laplace type are well-known. In particular,

- solutions of Eqs. 1.61 are sums of their partial solutions,
- the product of a partial solution of any Eq. 1.61 by an arbitrary constant also will be a solution of this equation.

These properties allow us to apply the superposition principle, which is widely used for solving the Laplace equation. Thus, if potential functions φ_1, φ_2 etc. or stream functions ψ_1, ψ_2 etc. satisfy the Laplace equation, the solution of the problem can be represented as

$$\varphi = \varphi_1 + \varphi_2 + \dots, \quad \psi = \psi_1 + \psi_2 + \dots \quad (1.62)$$

To use the superposition principle, one needs to write relationships for functions φ and ψ in the basic coordinate systems. Such relationships are:

- in the Cartesian coordinate system, Cauchy–Riemann Eq. 1.60 written in the form

$$q_x = -\frac{\partial \varphi}{\partial x} = -\frac{\partial \psi}{\partial y}, \quad (1.63a)$$

$$q_y = -\frac{\partial\varphi}{\partial y} = \frac{\partial\psi}{\partial x}; \quad (1.63b)$$

– in the cylindrical (axisymmetric) coordinate system:

$$q_r = -\frac{\partial\varphi}{\partial r} = -\frac{1}{r} \frac{\partial\psi}{\partial\theta}, \quad (1.64a)$$

$$q_\theta = -\frac{1}{r} \frac{\partial\varphi}{\partial\theta} = \frac{\partial\psi}{\partial r}. \quad (1.64b)$$

Next expressions for typical flow structures that form under the effect of regional flow or isolated sources of hydrodynamic perturbations are to be obtained. Let us consider some simple example, well described in fundamental studies of some authors (see, e.g., (Bear 1972; Javandel et al. 1984)).

In the case of a *one-dimensional flow* with a specific discharge of q_0 , whose vector forms an angle α with the x axis,

$$q_x = q_0 \cos \alpha, \quad q_y = q_0 \sin \alpha, \quad (1.65)$$

and, considering (1.63), we have

$$\varphi = \varphi_0 - q_0 (x \cos \alpha + y \sin \alpha), \quad (1.66a)$$

$$\psi = \psi_0 - q_0 (y \cos \alpha - x \sin \alpha). \quad (1.66b)$$

In the case of a *radial flow* formed by an injection well with a flow rate of Q_w [L^3T^{-1}], in accordance with (1.64) we have

$$q_r = \frac{Q_w}{2\pi m r} = -\frac{\partial\varphi}{\partial r} = -\frac{1}{r} \frac{\partial\psi}{\partial\theta}. \quad (1.67)$$

Integrating (1.67), we obtain

$$\varphi = \varphi_0 - \frac{Q_w}{2\pi m} \ln r, \quad \psi = \psi_0 - \frac{Q_w}{2\pi m} \theta, \quad (1.68)$$

or, in the Cartesian coordinate system:

$$\varphi = \varphi_0 - \frac{Q_w}{4\pi m} \ln(x^2 + y^2), \quad (1.69a)$$

$$\psi = \psi_0 - \frac{Q_w}{2\pi m} \arctg\left(\frac{y}{x}\right). \quad (1.69b)$$

1.2.2.2 Basic Characteristic Solutions

The obtained analytical expressions, relating specific discharge components q_x and q_y with functions φ and ψ , allow the motion equations of fluid particles in curvilinear coordinates to be represented in several forms.

Thus, since the projections of u_x and u_y (principal components of the transport velocity vector) onto coordinate axes are dx/dt and dy/dt , the equations for the projections of the Darcy specific discharge can be represented as

$$q_x = \phi \frac{dx}{dt}, \quad q_y = \phi \frac{dy}{dt}. \quad (1.70)$$

Separating variables in (1.70) and integrating these equations, considering (1.54) and (1.54), we obtain the following equations of motion of fluid particles in the directions of x and y :

$$t = -\phi \int_{x_0}^x \frac{1}{\partial\psi/\partial y} dx, \quad t = -\phi \int_{y_0}^y \frac{1}{\partial\psi/\partial x} dy. \quad (1.71)$$

Another approach to the construction of migration calculation models in curvilinear coordinates involves the search for characteristic solutions of the generalized equation of advective transport (1.25), which in the case of $W_f = 0$ and $W_s = 0$ takes the form

$$\phi \frac{\partial C(x, y, t)}{\partial t} + \mathbf{q} \cdot \nabla C(x, y, t) = 0. \quad (1.72)$$

To describe variations in the concentration function in curvilinear coordinates (relative to the original x - y system), we will use the series of operations:

$$\begin{aligned} \mathbf{q} \cdot \nabla C &= q_x(x, y) \frac{\partial C}{\partial x} + q_y(x, y) \frac{\partial C}{\partial y} = \nabla \varphi \cdot \nabla C = \nabla \varphi \cdot \left(\frac{\partial C}{\partial \varphi} \nabla \varphi + \frac{\partial C}{\partial \psi} \nabla \psi \right) \\ &= (\nabla \varphi)^2 \frac{\partial C}{\partial \varphi} + \nabla \varphi \nabla \psi \frac{\partial C}{\partial \psi}. \end{aligned} \quad (1.73)$$

Because the functions φ and ψ are conjugate, we finally have

$$\mathbf{q} \cdot \nabla C = q^2(\varphi, \psi) \frac{\partial C}{\partial \varphi}, \quad (1.74)$$

where

$$q^2(\varphi, \psi) = \left(\frac{\partial \varphi}{\partial x} \right)^2 + \left(\frac{\partial \varphi}{\partial y} \right)^2 = q_x^2 + q_y^2. \quad (1.74a)$$

In this case, advection transport Eq. 1.72 takes the quasi-one-dimensional form:

$$\phi \frac{\partial C}{\partial t} + q^2(\varphi, \psi) \frac{\partial C}{\partial \varphi} = 0. \quad (1.75)$$

The characteristic solution for Eq. 1.75 can be presented in the form

$$dC = 0 \text{ along } t - \phi \int_{\varphi_0}^{\varphi} \frac{d\varphi'}{q^2(\varphi', \psi)} = \text{const}, \quad (1.76)$$

similar to solution (1.50); here φ_0 and φ are potentials in the point of the initial and final positions of the particle on the streamline ψ .

1.2.2.3 Particular Examples

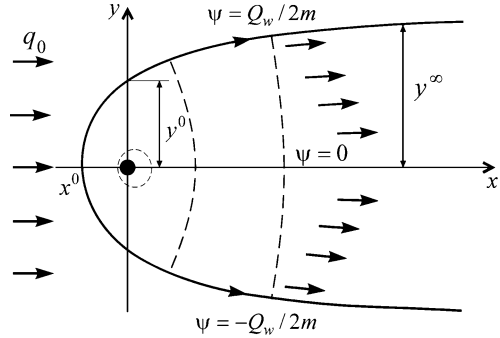
Solutions for basic functions φ and ψ , similar to (1.66) and (1.69), are used to find more general solutions, reflecting the superposition of several factors of hydrodynamic perturbation in aquifers. The subsequent integration of appropriate functions allows us to find time characteristics for describing the motion of concentration fronts. The theoretical basis for studies of this type is well-developed, and many examples can be found in the appropriate scientific literature, describing the structure of flows that form in the subsurface media under the effect of hydrodynamic interaction of well systems both in the presence and in the absence of natural groundwater flow, or when wells are operated near natural hydrodynamic boundaries (Strack 1989; Charbeneau 2000).

The approach considered above is especially effective in determining the configuration of the boundaries (in the x - y plane), within which water in an aquifer moves toward pumping-out wells against the background of natural (regional) flow. These boundaries are associated with the planar position of neutral (water-dividing) streamlines ψ_{capt} enclosing the so-called capture zones. The calculation of the planar position of the appropriate lines $\psi_{\text{capt}}(x, y)$ or individual characteristic points is directly related to the determination of boundaries of wellhead (sanitary) protection zones.

Similar formulation is typical of the problems posed to substantiate active water-protection measures involving the use of pumping-out or injection wells. For example, this may include evaluating the effect of a row of drainage (unwatering) wells aimed to intercept polluted-groundwater flow threatening a facility, which is to be protected (Kauch 1982; Javandel and Tsang 1986). The distance between the wells should be chosen so as to form a single flow-dividing line, separating them from the regional flow and ensuring that the facility further downstream is protected against pollution. The effect of injection wells used to form hydrodynamic barriers can be calculated in a similar manner.

As a *first example*, let us consider the problem of motion of the boundary between a replacing liquid and a liquid being replaced when a solution is being pumped into a well against the background of natural groundwater flow (Fig. 1.3).

Fig. 1.3 Injection well in a natural flow (the contour shown by a *full* line is the neutral streamline, *dashed* are equipotential lines)



The superposition of basic solutions for linear flow ((1.66) ($\alpha = 0$) and (1.69)) yields

$$\varphi = \varphi_0 - q_0 x - \frac{Q_w}{4\pi m} \ln(x^2 + y^2), \quad (1.77a)$$

$$\psi = \psi_0 - q_0 y - \frac{Q_w}{2\pi m} \operatorname{arctg}\left(\frac{y}{x}\right), \quad (1.77b)$$

where q_0 is the specific discharge of the regional flow [LT^{-1}]; Q_w is the volumetric flow (injection) rate [L^3T^{-1}]; φ_0 and ψ_0 are integration constants (in the accepted coordinate system, it is convenient to use the “zero” stream line $y = 0$ $\psi = 0$ as the reference, such that $\psi_0 = 0$) [L^2T^{-1}].

From Eq. 1.77a, one can readily obtain expressions for the components of real flow velocity:

$$u_x = \frac{q_x}{\phi} = -\frac{1}{\phi} \frac{\partial \varphi}{\partial x} = \frac{dx}{dt} = \frac{q_0}{\phi} + \frac{Q_w}{2\pi m \phi} \frac{x}{x^2 + y^2}, \quad (1.78a)$$

$$u_y = \frac{q_y}{\phi} = -\frac{1}{\phi} \frac{\partial \varphi}{\partial y} = \frac{dy}{dt} = \frac{Q_w}{2\pi m \phi} \frac{y}{x^2 + y^2}. \quad (1.78b)$$

The joint analysis of the differential part of identity (1.78b) and equation for streamline (1.77b) yields the expression (at $\psi_0 = 0$), relating the differential of time (dt) with an elementary increment of the coordinate (dy):

$$dt = \frac{2\pi m \phi}{Q_w} \operatorname{cosec}^2 \left[\frac{2\pi m}{Q_w} (\psi + q_0 y) \right] y dy. \quad (1.79)$$

Integrating (1.79) yields the time required for the particle that started from the well ($x = 0$, $y = 0$) at $t = 0$ to reach point x , y (Bear 1972). The appropriate dimensionless solution has the form:

$$\tau = \xi + \ln \left(\frac{\sin \theta}{\sin(\eta + \theta)} \right), \quad (1.80)$$

where

$$\xi = \frac{2\pi m q_0}{Q_w} x, \quad \eta = \frac{2\pi m q_0}{Q_w} y, \quad \tau = \frac{2\pi m q_0^2}{\phi Q_w} t, \quad \theta = \arctg\left(\frac{\eta}{\xi}\right). \quad (1.80a)$$

From solution (1.80) we can derive, in particular, the equation describing the position of the front in the moment $\tau = \tau_0$ (Bear 1972):

$$\left(\cos \eta + \frac{\xi}{\eta} \sin \eta\right) \exp(-\xi) = \exp(\tau_0) = \text{const.} \quad (1.81)$$

The obtained relationships describe, in essence, all features of the structure of the flow field formed by the injection well in a natural flow. Thus, at $\tau \rightarrow \infty$, we have the expression for calculating the position of the flow-dividing line:

$$\xi = -\frac{\eta}{\text{tg } \eta}, \quad (1.82)$$

whence we can determine all characteristic points of the neutral streamline; for example, the maximal displacement of the front along the x -axis against the flow is governed by the value

$$x^0 = x \Big|_{y=0} = -\frac{Q_w}{2\pi m q_0}, \quad (1.83a)$$

(this expression can be directly derived from expression for the potential function (1.77a): $\partial\varphi(x, 0)/\partial x = 0$) and that along the y -axis, by the values

$$y^0 = y \Big|_{x=0} = \pm \frac{Q_w}{4m q_0} \quad \text{and} \quad y^\infty = y \Big|_{x=\infty} = \pm \frac{Q_w}{2m q_0}, \quad (1.83b)$$

i.e., $y^\infty = 2y^0$. The velocity of front migration along the $\xi(x)$ axis is described by

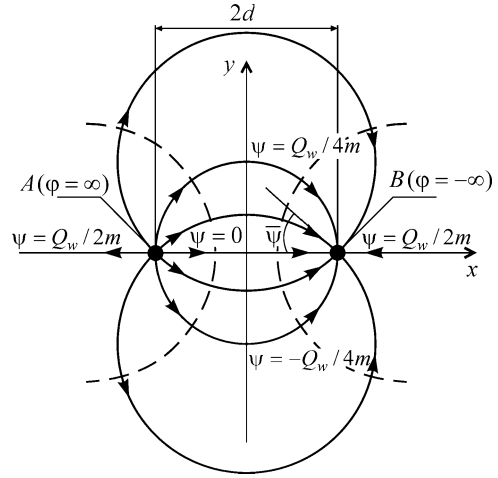
$$\tau = \xi - \ln(1 + \xi), \quad (1.84)$$

which can be used to calculate the coordinates x of the front both upstream and downstream of the groundwater flow. It can be easily shown that at $q_0 t / \phi x^0 < 0.1$, the configuration of the front is close to a circle, while at $q_0 t / \phi x^0 > 1$ it tends to an ellipse. In the latter case, the motion of particles in x direction (at $y = 0$) is adequately described by the formula (Ceric and Haitjema 2005):

$$\xi = \tau + \ln(\tau + e), \quad e = 2.718. \quad (1.85)$$

The second example, illustrating the advantages of the approach under consideration is the solution of the problem for *dipole* system of equal-rate wells – a pumping-out and an injection ones – separated by a distance $2d$ (Muskat 1937; Bear 1972; Eldor and Dagan 1972; Javandel et al. 1984). The wells are supposed to be

Fig. 1.4 Layout of wells with respect to coordinate axes: dipole-well system (*full* lines are streamlines, *dashed* are equipotential lines)



located on the x -axis (Fig. 1.4) in points $(\pm d, 0)$, while the y -axis is orthogonal to the x axis and passes midway between the wells. The problem is to find the migration trajectories of water particles, starting from the line $x = 0$, toward the pumping-out well, and to calculate the time required for these particles to reach any point in the half-plane $x > 0$.

The superposition of basic solutions (1.69) for a double-well system yields the following equations for potential function φ and stream function ψ :

$$\varphi = \varphi_0 + \frac{Q_w}{4\pi m} \ln \frac{y^2 + (x-d)^2}{y^2 + (x+d)^2}, \quad (1.86a)$$

$$\psi = \psi_0 + \frac{Q_w}{2\pi m} \left[\arctg\left(\frac{y}{x-d}\right) - \arctg\left(\frac{y}{x+d}\right) \right], \quad (1.86b)$$

where Q_w is the volumetric flow rate of each well, φ_0 is the value of the potential on the line $x = 0$. It is convenient to choose an integration constant ψ_0 so that the line running from the injection to pumping-out well will have a zero value.

By using relationships (1.86) we can easily show that both equipotential lines and streamlines are circumferences, tangents to which in their intersection points are perpendicular (Fig. 1.4). This provides a direct proof to the fact that the flow domain in curvilinear coordinates φ, ψ is a rectangle, in this case, with the lateral sides moved to infinity. The latter is due to the fact that the potential function φ takes the values $+\infty$ (injection well) and $-\infty$ (pumping-out well).

The specific discharge in curvilinear coordinates is related to functions $\varphi(x, y)$ and $\psi(x, y)$ in the following manner:

$$|q(\varphi, \psi)|^2 = |\nabla \varphi|^2 = \left(\frac{\partial \varphi}{\partial x}\right)^2 + \left(\frac{\partial \varphi}{\partial y}\right)^2 = q_x^2 + q_y^2 = \left(\frac{Q_w}{2\pi m d}\right)^2 (\operatorname{ch} \bar{\varphi} + \cos \bar{\psi})^2, \quad (1.87)$$

$$\bar{\varphi} = \frac{2\pi m(\varphi_0 - \varphi)}{Q_w}, \quad \bar{\psi} = \frac{2\pi m\psi}{Q_w}. \quad (1.87a)$$

The substitution of (1.87) into the integration term for the equation for characteristics (1.76) and the integration from φ_0 to φ yields an expression for determining the migration time of particles from boundary φ_0 along any trajectory φ to the given point with current coordinates φ, ψ (Bear 1972; Eldor and Dagan 1972). In the dimensionless form, the solution becomes:

$$\tau = \frac{1}{\sin^2 \bar{\psi}} \left[\frac{\text{sh } \bar{\varphi}}{\text{ch } \bar{\varphi} + \cos \bar{\psi}} - 2 \text{ctg } \bar{\psi} \cdot \arctg \left(\text{th } \frac{\bar{\varphi}}{2} \text{tg } \frac{\bar{\psi}}{2} \right) \right], \quad (1.88)$$

where $\tau = Q_w t / 2\pi m d^2 \phi$.

Assuming $\varphi = -\infty$, which corresponds to the potential in the point of the pumping-out well, we obtain the formula for dimensionless particle travel time from the initial linear contour $\varphi = \varphi_0$ to the well:

$$\tau = \frac{1}{\sin^2 \bar{\psi}} (1 - \bar{\psi} \text{ctg } \bar{\psi}). \quad (1.89)$$

For the shortest streamline $\bar{\psi} = 0$, we have $\tau = 1/3$. Note also that in the coordinate system used here, the tangent to the streamline with dimensionless value $\bar{\psi}$ in the point of the pumping-out well makes angle $\bar{\psi}$, with the x -axis ($y = 0$) (Fig. 1.4).

Clearly, the hydrodynamic effect of functioning of two equal-rate wells, which maintain constant potential (head) on the line $x = 0$, is equivalent, for the half-plane $x > 0$, to the effect of functioning of a pumping-out well near a feeding boundary of the first-type (represented, for example, by a “perfect” river).

1.3 A One-Dimensional Model of Microdispersion

From the viewpoint of the significance of microdispersion effects at different scales of solute migration analysis and as an illustration of principles of solution of appropriate boundary problems, of particular interest is the analysis of the one-dimensional equation

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} - D_L \frac{\partial^2 C}{\partial x^2} = 0, \quad (1.90)$$

which is a particular case of the general mass balance equation in a flow in porous medium (1.25). The transformation of (1.25) to the one-dimensional form (1.90) implies that neglected are the transport components orthogonal to the vector of mean flow velocity $q \equiv q_x$, as well as the sources ($W_f = 0$ and $W_s = 0$). The coefficient of longitudinal dispersion D_L in this case is determined by (1.22).

A number of closed-form solutions of (1.90) for different types of boundary conditions are available in the literature on both hydrogeology and chemical-reaction engineering. Many of them were compiled by van Genuchten and Alves (1982),

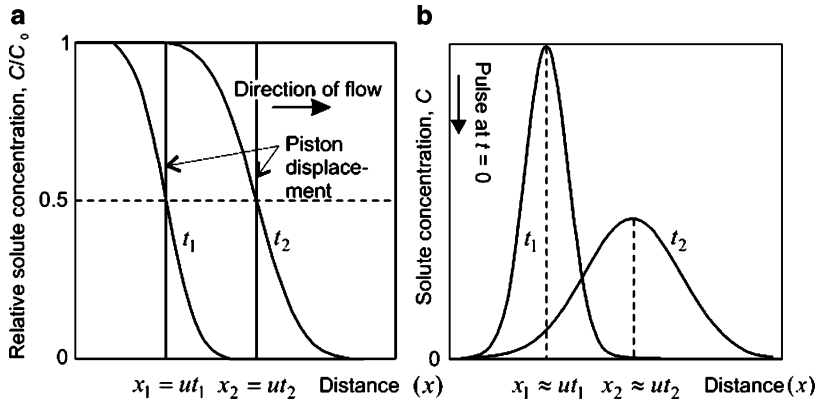


Fig. 1.5 Solute spatial distribution due to 1D advection and dispersion at time t_1 and t_2 for continuous (a) and pulse (b) releases if the average groundwater velocity is u

Toride with co-authors (1995) and others. Traditionally, differential equation (1.90) is solved with Heaviside step function or Dirac delta function (impulse function) taken as basic input signals (Fig. 1.5). The corresponding solutions can be adapted to describe other forms of input concentration signals (functions). The solutions given below describe solute migration in an infinite ($-\infty < x < \infty$) and semibounded ($0 \leq x < \infty$) domains.

1.3.1 Solutions for Infinite Porous Domain

The simplest, though the most widely used in practice is the approximate solution of Eq. 1.90 that can be derived from the following considerations. Suppose that at the initial moment ($t = 0$), two liquids containing some conservative tracer in concentration $C = C_0$ at $x < 0$ and $C = 0$ at $x > 0$ are in contact in point $x = 0$. Conventionally, we can suppose that at $x = 0$ $C = C_0/2$. Appropriately formalized, the boundary conditions take the form:

$$C(x, 0) = C_0 H(-x), \quad -\infty < x < \infty; \quad (1.91a)$$

$$C(-\infty, t) = C_0, \quad t > 0, \quad C(+\infty, t) = 0, \quad t > 0, \quad (1.91b)$$

where $H(-x)$ is step *Heaviside function*, written for the space coordinate:

$$H(-x) = 1, \quad x < 0; \quad H(-x) = 1/2, \quad x = 0; \quad H(-x) = 0, \quad x > 0. \quad (1.91c)$$

Consider the process in the moving coordinate system

$$\eta = x - ut, \quad \tau = t \quad (u = q/\phi). \quad (1.92)$$

Now the derivatives in Eq. 1.90 can be rewritten with the use of the chain rule of differentiation of a superposition of functions:

$$\frac{\partial C}{\partial x} = \frac{\partial C}{\partial \eta} \frac{\partial \eta}{\partial x} + \frac{\partial C}{\partial \tau} \frac{\partial \tau}{\partial x} = \frac{\partial C}{\partial \eta} (1) + \frac{\partial C}{\partial \tau} (0) = \frac{\partial C}{\partial \eta}, \quad \frac{\partial^2 C}{\partial x^2} = \frac{\partial^2 C}{\partial \eta^2}, \quad (1.93a)$$

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial \eta} \frac{\partial \eta}{\partial t} + \frac{\partial C}{\partial \tau} \frac{\partial \tau}{\partial t} = \frac{\partial C}{\partial \eta} (-u) + \frac{\partial C}{\partial \tau} (1) = \frac{\partial C}{\partial \tau} - u \frac{\partial C}{\partial \eta}. \quad (1.93b)$$

Substitute the obtained relationships for partial derivatives (1.93) into (1.90). The result is the diffusion-type equation

$$\frac{\partial C}{\partial \tau} - D_L \frac{\partial^2 C}{\partial \eta^2} = 0. \quad (1.94)$$

Thus, near the front moving with constant velocity u , we have symmetrical dispersion, resulting in the redistribution of solutes both left ($\eta < 0$) and right ($\eta > 0$) of the replacement front. In virtue of such symmetry, the concentration on the front is $C = C_0/2$. The fundamental solution of diffusion equation (1.94) under condition $C(\eta = 0, t) = C_0/2$ is well known:

$$C(\eta, \tau) = \frac{C_0}{2} \operatorname{erfc} \left(\frac{\eta}{\sqrt{4D_L \tau}} \right). \quad (1.95)$$

Returning to the initial coordinate system (x, t) , we finally obtain

$$\bar{C} = \frac{C}{C_0} = \frac{1}{2} \operatorname{erfc}(\xi). \quad (1.96)$$

Here

$$\xi = \frac{x - ut}{\sqrt{4D_L t}}; \quad (1.96a)$$

$\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty \exp(-z'^2) dz'$ is erfc function, $\operatorname{erfc}(z) = 1 - \operatorname{erf}(z)$; $\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-z'^2) dz'$ is probability integral (error function integral).

Let us consider the basic properties of function $\operatorname{erfc}(z)$, which is tabulated in many special mathematical publications and the hydrogeological literature:

$$\operatorname{erfc}(-z) = 2 - \operatorname{erfc}(z), \quad \operatorname{erfc}(0) = 1, \quad \operatorname{erfc}(\infty) = 0, \quad \operatorname{erfc}(-\infty) = 2. \quad (1.97)$$

Actually, the symmetry of the concentration distribution about the space coordinate $x_0 = ut$ is violated due to solute dispersion through the interface at the initial moment $t = 0$, the fact that can be accounted for in the boundary conditions (Leij and Toride 1995):

$$C(x, 0) = C_0 H(-x) \left[1 + \frac{2D_L}{u} \delta(x) \right] - \infty < x < \infty, \quad (1.98a)$$

$$C(-\infty, t) = C_0, \quad t > 0; \quad C(+\infty, t) = 0, \quad t > 0; \quad (1.98b)$$

here $\delta(x)$ is delta function. Thus stated, the problem's solution has the form:

$$\bar{C} = \frac{1}{2} \left[\operatorname{erfc}(\xi) + \sqrt{\frac{D_L}{\pi u^2 t}} \exp(-\xi^2) \right], \quad (1.99)$$

where complex argument $\xi = \xi(x, t)$ is defined in accordance with (1.96a).

1.3.2 A Basic (Fundamental) Solution for Semi-Infinite Porous Domain

Solutions describing chemical transport for a semi-infinite soil column or field soil profile are the most asked-for in hydrogeologic practice. A simplified formulation involves a first-type (Dirichlet) boundary condition on the upstream boundary ($x = 0$), neglecting the dispersion component of the input mass flow:

$$C(0, t) = C_0 H(t), \quad t > 0, \quad (1.100a)$$

where $H(t)$ is the Heaviside step function written for the time (also called the unit step function). Additionally, we specify a condition on the remote boundary and a zero initial condition:

$$C(+\infty, t) = 0; \quad (1.100b)$$

$$C(x, 0) = 0, \quad 0 < x < \infty. \quad (1.100c)$$

Upon changing concentration function $C(x, t)$ in (1.90) to new dependent variable $G(x, t)$ defined as

$$C(x, t) = G(x, t) \exp\left(\frac{ux}{2D_L} - \frac{u^2 t}{4D_L}\right), \quad (1.101)$$

we obtain the diffusion equation:

$$\frac{\partial G}{\partial t} - D_L \frac{\partial^2 G}{\partial x^2} = 0. \quad (1.102)$$

Conditions (1.100) become

$$G(0, t) = C_0 \exp(u^2 t / 4D_L), \quad (1.103a)$$

$$G(+\infty, t) = 0, G(x, 0) = 0. \quad (1.103b)$$

A solution of the system (1.102)–(1.103) is given by [Lapidus and Amundson \(1952\)](#), [Ogata and Banks \(1961\)](#) and can be presented in the form

$$\bar{C} = \frac{1}{2} [\operatorname{erfc}(\xi) + e^{\operatorname{Pe}} \operatorname{erfc}(\xi')] \quad (1.104)$$

often referred to as the basic (or *fundamental*) solution of 1D advection–dispersion solute transport equation for step input. Here

$$\xi = \frac{x - ut}{\sqrt{4D_L t}} = \frac{1 - \bar{t}}{\sqrt{4\bar{t}/\operatorname{Pe}}}, \quad \xi' = \frac{x + ut}{\sqrt{4D_L t}} = \frac{1 + \bar{t}}{\sqrt{4\bar{t}/\operatorname{Pe}}}, \quad (1.104a)$$

$$\operatorname{Pe} = \frac{ux}{D_L}, \quad \bar{t} = \frac{t}{t_0}, \quad t_0 = \frac{x\phi}{q}. \quad (1.104b)$$

Analysis of solution (1.104) shows that, when $\operatorname{Pe} > 100 - 200$, the results of calculations based on it almost coincide with the approximate solution (1.96) for the infinite domain, which therefore may be taken as an approximation for the first term in the solution (1.104). Thus, formally, the second term in solution (1.104) can be regarded as a correction introduced to ensure the fulfillment of the Dirichlet boundary condition (at $x = 0$) for the solution of problem (1.96) in an infinite medium ($-\infty \leq x \leq \infty$). In other words, the second term arises from the influence of the inflow boundary condition (1.100a), producing a shift of the position of the concentration front for (1.96).

Formula (1.96) yields the equation of motion for any isoline with concentration $\bar{C}$ near the transport front:

$$x_{\bar{C}} = ut \pm 2 |\xi(\bar{C})| \sqrt{D_L t}, \quad (1.105)$$

where $\xi(\bar{C}) = \operatorname{inerfc}(2\bar{C})$ (see (1.96a)); the minus and plus signs refer to concentrations $\bar{C} > 0.5$ and $\bar{C} < 0.5$, respectively

Formula (1.105) can be used, in particular, to assess the length Δx of the transitional (dispersion) zone between the replacing solution and the solution being replaced (Fig. 1.5a). For example, the length of the dispersion zone in the range of relative concentrations $1\% \leq \bar{C} \leq 99\%$ is

$$\Delta x = x_{\bar{C}=0.01} - x_{\bar{C}=0.99} = 6.6 \sqrt{D_L t} \approx 6.6 \sqrt{\delta_L x_0} \quad (1.106)$$

(x_0 is the coordinate of the front of piston-type displacement).

Basing on this relationship and associating t and x_0 with the characteristic time and space scales at which the process is considered, we can assess the significance of microdispersion in homogeneous single porosity media under different conditions. In this context, the following points are worth mentioning.

1. The width of the transition zone in relatively short domains, as is typical of laboratory and field tracer tests with sand soils, is commonly commensurable with the size of the flow domain. However, in the forecasts made for homogeneous sand aquifers, Δx is negligible relative to the flow domain size, and the position of the replacement front is fully determined by the advective component. Therefore, it makes sense to develop forecasts for such aquifers by using a simpler, piston-type displacement scheme, making *longitudinal*-dispersion parameters less significant for such forecasts. Exceptions are the cases of short-time input of limited volumes of high-toxicity pollutants into an aquifer.
2. Conversely, fractured rocks with negligible porosity of blocks feature considerable scatter of dissolved species because of hydrodynamic dispersion, and the transition zone size is commensurable with that of the transport domain in both field tests and model (regional scale) forecasts. Therefore, process description based on the piston-like displacement will be incomplete, so the dispersivity parameter δ_L will be required to make the forecast more reliable.
3. When the specific discharge is small, as is typical of low-permeability deposits, the mass transfer mostly take place in the form of diffusion or advection–diffusion. Therefore, in addition to the determination of δ_L , the pore diffusion coefficient, D_m (or the effective diffusion coefficient, D_e) is to be determined.

Overall, the Fickian advection–dispersion model considered here shows that the understanding of the significance of individual solute transport components (mechanisms) is a critical aspect of the schematization of natural conditions, which is aimed to simplify the mathematical model of the process and determines the range of parameters required for calculations. The migration parameters, which adequately reflect the progress of processes under some conditions, are often of secondary significance for other conditions; moreover, the migration parameter values derived from tracer tests may differ from those adequately describing solute transport at the regional scale. That is why the choice of transport models is determined not only by the water-bearing rock complex and the conditions on aquifer boundaries, but also depends on space-time scales. To an even greater degree, as it will be shown in the following chapters, this aspect is important for selection and application of models developed for analysis of transport in dual porosity and heterogeneous systems.

1.3.3 On the Solution and Analysis of Solute Transport Problems by Applying the Laplace Transform

The solution of Eq. 1.90 with boundary condition (1.100) can also be obtained by operator method with the use of the *Laplace integral transform*. We will often use

this method for solving boundary value problems, therefore let us briefly consider the essence of this method and illustrate its application to the problem under consideration.

1.3.3.1 Basic Definitions

The integral (one-sided) Laplace transform

$$\tilde{C} = \tilde{C}(p) = \int_0^{\infty} C(t) \exp(-pt) dt \quad (1.107)$$

associates any single-valued function (original) $C(t)$ (t is a real variable, time) with a single function $\tilde{C}(p)$ (image) of complex variable $p = \sigma \pm i\alpha$.

In the solution of solute transport problems, the Laplace transform allows one to exclude partial derivative with respect to time and pass to ordinary differential equations that can be solved by standard methods. Successive transformation of original equations with respect to two independent variables t and x is also possible. The solutions expressed in terms of images for various input ($x=0$) concentration functions have similar analytical expressions, which differ in the form of the factor at solution kernels, all having the same type, i.e., *response functions*, which do not depend on the boundary conditions. This makes the procedure of search for generalized solutions and analytical passage from one type of boundary conditions to another much more simple.

Upon the solution of the boundary value problem in terms of images, the passage to the original will be generally implemented by the formula:

$$C(t) = \frac{1}{2\pi i} \int_{\sigma - i\infty}^{\sigma + i\infty} \tilde{C}(p) \exp(pt) dp; \quad (1.108)$$

here σ is a positive constant, $i = \sqrt{-1}$, i.e., the return to the domain of the original involves contour integration in the complex plane (Ditkin and Prudnikov 1965; Govindaraju and Das 2007).

A series of precalculated analytical expressions have been published, allowing one to implement direct and inverse transforms when searching for solutions with the help of the operation method (see, for example, Doetsch 1967, 1974; Bateman and Erdelyi 1954; van Genuchten and Alves 1982).

There exist well-developed *numerical methods for inverse Laplace transform* from the solutions in terms of images to originals of the functions being sought for (Stehfest 1970; Talbot 1979; Abate and Valkó 2004); these methods have been tested in the solution of various migration problems (Moench and Ogata 1981; Moench 1989, 1991, 1995; Becker and Charbeneau 2000; Tomasko et al. 2001; Reimus et al. 2003; Boupfa et al. 2004; Chen et al. 2007). Standard programs are available for such cases in applied mathematical program packages, such as *Mathematica*, *MathCad*, *MathSoft* and *Maple*. Those procedures are especially effective when

used to process the results of indicator (tracer) tests in aquifers by solving migration-related boundary value problems in Laplace images for various forms of concentration signals with some complicating factors taken into account (Chap. 7).

1.3.3.2 Examples (Particular Solutions of the Solute Transfer Problem)

With zero initial condition (1.100c), the Laplace transform (1.107) of the original Eq. 1.90 is an ordinary homogeneous second-order differential equation:

$$\frac{d^2 \tilde{C}}{d\eta^2} - 2a \frac{d\tilde{C}}{d\eta} - p\tilde{C} = 0, \quad (1.109)$$

where $\eta = \frac{x}{\sqrt{D_L}}$, $a = \frac{u}{2\sqrt{D_L}}$ $\left(a\eta = \frac{Pe}{2}\right)$.

The general solution of the Eq. 1.109 has the form

$$\tilde{C} = A \exp(a\eta) \exp\left(-\eta\sqrt{p+a^2}\right) + B \exp(a\eta) \exp\left(\eta\sqrt{p+a^2}\right), \quad (1.110)$$

where A and B are parametric (independent of x) functions, determined by the type of conditions at the boundary of the domain.

Thus, under the conditions of the fundamental problem, the boundary conditions (1.100a) and (1.100b) will be transformed into

$$\tilde{C}(0, p) = \frac{C_0}{p}, \quad (1.111a)$$

$$\tilde{C}(+\infty, p) = 0. \quad (1.111b)$$

The boundary condition (1.111b) will be satisfied only when $B = 0$, i.e.,

$$\tilde{C} = A \exp(a\eta) \exp\left(-\eta\sqrt{p+a^2}\right). \quad (1.112)$$

Now, equating η to zero, by virtue of condition (1.111a) on the inlet boundary, we obtain $A = C_0/p$. Thus, the final solution of the problem in Laplace images takes the form:

$$\tilde{C} = \frac{C_0}{p} \exp\left(-\eta(\sqrt{p+a^2} - a)\right). \quad (1.113)$$

The inverse transform of (1.113) can be obtained by using several approaches based on well-known relationships and rules of the operator calculus (Doetsch 1967; Bateman and Erdelyi 1954; Govindaraju and Das 2007). Thus, since in accordance with the theorem on convolution of functions we have

$$L^{-1} \left[\frac{1}{p} \tilde{f}(p) \right] = \int_0^t f(\tau) d\tau, \quad (1.114a)$$

then, performing successive operations

$$L^{-1} \left[e^{-\eta \sqrt{p}} \right] = \frac{\eta}{2\sqrt{\pi t}^{3/2}} e^{-\eta^2/4t}, \quad (1.114b)$$

$$L^{-1} \left[e^{-\eta \sqrt{p+a^2}} \right] = \frac{\eta}{2\sqrt{\pi t}^{3/2}} e^{-a^2 t} e^{-\eta^2/4t} \quad (1.114c)$$

(transform lag theorem) and

$$L^{-1} \left[e^{a\eta} e^{-\eta \sqrt{p+a^2}} \right] = \frac{\eta}{2\sqrt{\pi t}^{3/2}} e^{-\eta^2/4t - a^2 t + a\eta}, \quad (1.114d)$$

we come to the *fundamental solution* of the problem in the integral form:

$$\bar{C} = \frac{x}{2\sqrt{\pi D_L}} \int_0^t \frac{1}{\tau^{3/2}} \exp \left[-\frac{(x - u\tau)^2}{4D_L \tau} \right] d\tau. \quad (1.115)$$

After additional algebraic operations, we obtain the fundamental solution (1.104), where:

$$\xi = \frac{\eta}{2\sqrt{t}} - a\sqrt{t}, \quad \xi' = \frac{\eta}{2\sqrt{t}} + a\sqrt{t}, \quad \text{Pe} = 2a\eta = \frac{ux}{D_L}. \quad (1.116)$$

Along with the solution (1.104), derived for step input (1.100b), widely used in hydrogeological calculations are solutions for pulse input (discontinuous signal), concentration parcel (square-wave pulse), and exponentially decaying input concentration signal, respectively,

$$C(0, t) = \frac{M}{\phi u S} \delta(t), \quad t > 0, \quad (1.117)$$

$$C(0, t) = \begin{cases} C_0 & 0 \leq t \leq t_s, \\ 0 & t > t_s, \end{cases} \quad (1.118)$$

$$C(0, t) = C_0 \exp(-\gamma t), \quad t > 0, \quad (1.119)$$

where M is the injected mass [M], S is flow cross-section area [L²], $\delta(t)$ is Dirac delta function [T⁻¹], t_s is the duration of the period within which the concentration at the boundary $x = 0$ was maintained constant, γ is some empirical coefficient, the form of which depends on the character of the problem to be solved.

In the case of pulse signal (Eq. 1.117, Fig. 1.5b), by analogy with the step input, we obtain $A = M/qS$, so that the inversion of formula (1.112) yields (Lenda and Zuber 1970; Zuber 1974; Leij and Toride 1995):

$$\bar{C}_i \equiv \frac{\phi C_i S x}{M} = \frac{1}{\sqrt{\frac{4\pi}{\text{Pe}} \bar{t}^3}} \exp \left[-\frac{(1 - \bar{t})^2}{\frac{4}{\text{Pe}} \bar{t}} \right]. \quad (1.120)$$

Solution (1.120) corresponds to the flux concentration (C_F , see Sect. 1.1.3), measured in a fluid in the outlet section (Kreft and Zuber 1979). It most adequately describes the conditions of experimental measurements, which are most often (except when remote control is involved) encountered in the practice.

It can be easily seen that the images of solutions for concentrations C and C_i are related by

$$\frac{\tilde{C}}{C_0} = \frac{1}{p} \frac{\phi u S}{M} \tilde{C}_i, \quad (1.121)$$

whence, by using the convolution theorem (Doetsch, 1967), we obtain

$$\frac{C}{C_0} = \frac{\phi u S}{M} \int_0^t C_i dt, \text{ or } \tilde{C} = \int_0^{\bar{t}} \tilde{C}_i d\bar{t}. \quad (1.122)$$

An alternative form, following from (1.122), is

$$\frac{d\tilde{C}}{d\bar{t}} = \tilde{C}_i \equiv \frac{\phi C_i S x}{M}, \quad (1.123)$$

i.e., dimensionless concentration $\tilde{C}_i$ is the derivative of function $\tilde{C}$ with respect to dimensionless time $\bar{t}$.

One can easily see that the integration of function (1.120) yields (1.115), which is equivalent to the fundamental solution (1.104). Note also that relative concentration $\tilde{C}_i$ is the ratio of the current concentration C_i to concentration $C_0 = M/V$, where $V = \phi S x$ is the volume of the void space in the fluid-saturated matrix between the section of solute input (instantaneous injection) into the aquifer and observation point x .

In the case of square-wave and exponentially decaying input signals, parametric functions A in the equation are defined as follows:

$$A = \frac{C_0}{p} [1 - \exp(-t_s p)], \quad A = \frac{C_0}{p + \gamma}. \quad (1.124)$$

The substitution of the first expression (1.124) into operation solution (1.112) allows the shift theorem to be applied (Doetsch 1967), according to which the required solution for a square concentration pulse is a superposition of basic functions of fundamental solution (1.104):

$$C_s(x, t) = \begin{cases} C(x, t) & \text{when } t \leq t_s, \\ C(x, t) - C(x, t - t_s) & \text{when } t > t_s. \end{cases} \quad (1.125)$$

Thus, we see that the core of operator solution (1.112), determined by two exponential factors in its right part, is a response function to a perturbation of any shape in the description of one-dimensional microdispersion in a semi-bounded domain. Parametric function A is the response to the boundary condition.

Note also that the solutions given above have been obtained for a Dirichlet boundary condition at the inlet flow boundary, where the diffusion (dispersion) solute transport component is neglected. Therefore, the description of solute migration in aquifer with relatively low permeability, where advection and diffusion solute fluxes may require the use of other solutions of boundary value problems (van Genuchten 1981; van Genuchten and Alves 1982; Lindstrom and Boersma 1989), obtained with the use of a more strict, third-type boundary condition, e.g., (1.29), which can be represented as

$$\left(C - \frac{D_L}{u} \frac{\partial C}{\partial t} \right) \Big|_{x=0^+} = C_0 H(t), \quad t > 0. \quad (1.126)$$

The solution in images holds its shape (1.112) at

$$A = \frac{C_0}{p} \frac{2a}{a + \sqrt{p + a^2}} \equiv \frac{C_0}{p} \frac{2}{1 + \sqrt{1 + 4D_L p / u^2}}. \quad (1.127)$$

The inversion of formula (1.112) yields the solution (Brenner 1962; Gershon and Nir 1969; Leij and Toride 1995):

$$\bar{C} = \frac{1}{2} \left\{ \operatorname{erfc}(\xi) + \sqrt{\frac{4 \operatorname{Pe} \bar{t}}{\pi}} e^{-\xi^2} - [1 + \operatorname{Pe}(1 + \bar{t})] e^{\operatorname{Pe}} \operatorname{erfc}(\xi') \right\}, \quad (1.128)$$

where ξ and ξ' are defined by (1.104a) and can be represented as functions of dimensionless variables Pe (1.104b) and $\bar{t} = ut/x$.

Analysis of solution (1.128) shows that the maximal concentration $\bar{C} = 1$ at the inlet boundary ($x \rightarrow 0$) is attained not instantaneously and depends on dimensionless group $\operatorname{Pe} \bar{t} = u^2 t / D_L$ (Gershon and Nir 1969; van Genuchten and Alves 1982). Physically, such gradual increase in the concentration can be attributed to the fact that at the beginning of the process (approximately, while $t < 10D_L/u^2$), the diffusion term is commensurable with the advection term or even exceeds it because of the large concentration gradient.

The mathematical formalization of the process that proceeds in the short segment $0 \leq x \leq L$ (tentatively, when the characteristic number $\operatorname{Pe} = uL/D_L < 10$) implies that Cauchy condition will also be specified on the outlet boundary ($x = L$) of the flow (Gershon and Nir 1969).

1.3.3.3 Connection with Statistical Moments

Solving migration problems in Laplace transforms allows one to obtain analytical solutions not only for the required concentration functions but also for their integral characteristics – statistical (temporal) moments. The relationship between statistical moments

$$m_n = \int_0^\infty t^n C(t) dt. \quad (1.129)$$

(n is the moment's order) of breakthrough concentration functions $C(t)$ obtained for an impulse input signal and the solution of the problem in Laplace images $\tilde{C}(p)$ is established by the equality (Van der Laan 1958; Verigin et al. 1977; Jönsson 1984; Veling 2005; Govindaraju and Das 2007)

$$m_n = (-1)^n \left. \frac{\partial^n \tilde{C}}{\partial p^n} \right|_{p \rightarrow 0}. \quad (1.130)$$

From here, we have, for example,

$$\theta = \frac{m_1}{m_0} = - \lim_{p \rightarrow 0} \frac{1}{\tilde{C}} \frac{\partial \tilde{C}}{\partial p} \quad (1.131)$$

- the expectation, characterizing the mean travel time (static position of the center of gravity of curve, $C(t)$) [T],

$$\sigma_t^2 = \frac{m_2}{m_0} - \theta^2 = \lim_{p \rightarrow 0} \frac{1}{\tilde{C}} \frac{\partial^2 \tilde{C}}{\partial p^2} - \theta^2 \quad (1.132)$$

- the variance of travel times (mean-square deviation), which characterizes the degree of dispersion of the points of curve $C(t)$ about the mean [T²].

Thus, solution in Laplace transforms (1.112) at $A = M/qS$ establishes the following relationship between temporal moments and the coefficients of the original differential Eq. 1.104:

$$\bar{\theta} = 1 + \text{Pe}^{-1}, \quad \bar{\sigma}_t^2 = 2\text{Pe}^{-1} + 3\text{Pe}^{-2}. \quad (1.133)$$

where $\bar{\theta} = \theta/t_0$, $\bar{\sigma}_t^2 = (\sigma/t_0)^2$; t_0 and Pe are defined by (1.104b); in this case,

$$\theta = \frac{\int_0^\infty t C(t) dt}{\int_0^\infty C(t) dt}, \quad \sigma_t^2 = \frac{\int_0^\infty (t - \theta)^2 C(t) dt}{\int_0^\infty C(t) dt}. \quad (1.134)$$

The approach of temporal moments is an efficient tool for interpretation of the experimental data. For example, rather than using the entire concentration breakthrough curve, one may use the temporal moments of the breakthrough curve. In this case the latter is considered as a series of discrete determinations of concentration C_k at different times t_k . Thus, first temporal moment of the breakthrough curve is used to describe the mean travel time and the second central moment is used to describe the variance of travel times. Substituting these characteristics into normalized relationships, similar to (1.133), and solving the obtained system of equations, allows one to determine the solute transport parameters. For more complex solute transport

process including, for example, kinetically controlled mass transfer between the two domains the third moment is used to investigate the skewness of the breakthrough curve.

In addition, analysis of solutions of migration problems expressed in terms of temporal moments allows one to study the asymptotic behavior of a system and to obtain analytical expressions for effective solute transport parameters, by matching the moments to the analytical expressions derived for homogeneous transport models (Aris 1956; Chrysikopoulos et al. 1992; Hoehn and Santschi 1987; Lawrence et al. 2002; Govindaraju and Das 2007; Luo et al. 2008).

1.3.4 *Quasi-One-Dimensional Solution of Microdispersion Problems in Deformed Flows in Porous Media*

The obtained solutions for one-dimensional hydrodynamic dispersion can also be of use for studying migration processes in deformed (non-one-dimensional) flows. Thus, the general two-dimensional (in $x - y$ plane) advection–dispersion Eq. 1.25 can be reduced to a quasi-one-dimensional equation in a curvilinear coordinate system (Sect. 1.2.2). With this in view, one needs to use transform (1.74) and the identity (Bear 1972, p. 639)

$$\nabla \cdot (\mathbf{D} \cdot \nabla C) = q^2(\varphi, \psi) \frac{\partial}{\partial \varphi} \left(D_L \frac{\partial C}{\partial \varphi} \right), \quad (1.135)$$

which holds for a homogeneous porous medium, provided that the transverse dispersion exchange between adjacent streamlines can be neglected. The result is a mass balance equation in the form

$$\frac{\partial C}{\partial t} + u^2(\varphi', \psi') \frac{\partial C}{\partial \varphi'} - u^2(\varphi', \psi') \frac{\partial}{\partial \varphi'} \left(D_L \frac{\partial C}{\partial \varphi'} \right) = 0, \quad (1.136)$$

where $\varphi' = \varphi/\phi$, $\psi' = \psi/\phi$; here, the velocity $u^2(\varphi', \psi')$ is determined from (1.74a), and dispersion coefficient $D_L = \delta_L u(\varphi', \psi') + D_m$. In the initial Eq. 1.25, $W_f = 0$, $W_s = 0$. With appropriately averaged dispersion coefficient, quasi-one-dimensional solutions of the migration problem, similar to (1.104), can be obtained for the description of concentration fronts given the flow structure.

Migration in deformed flows in porous media can be analyzed with the use of another form hydrodynamic dispersion,

$$\frac{\partial C}{\partial t} + u(s) \frac{\partial C}{\partial s} - \delta_L u(s) \frac{\partial^2 C}{\partial s^2} = 0, \quad (1.137)$$

which reflects the conditions of particle motion along fixed trajectories (streamlines in Fig. 1.2), where s is the distance along streamline.

Some approximations following from the boundary-layer theory can be used to show (Gelhar and Collins 1971) that the variable (velocity-dependent) longitudinal dispersion coefficient is determined by the dispersivity constant and the mean displacement of the advective transport front. A series of transforms, based on the small-perturbation method, reduces Eq. 1.137 to the diffusion-type equation (Gelhar and Collins 1971; Welty and Gelhar 1994):

$$\frac{\partial C}{\partial \omega} - \delta_L \frac{\partial^2 C}{\partial \eta^2} = 0, \quad (1.138)$$

where

$$t_0(s) = \int_0^s \frac{ds'}{u(s')}, \quad \eta = t_0(s) - t, \quad \omega(t) = \int_0^{\bar{s}} \frac{ds'}{u^2(s')}; \quad (1.138a)$$

here $t_0(s)$ is the time required for the front to reach the point s [T]; s' is the mean position of the front at moment $t_0(s)$, calculated from the condition $t_0(\bar{s}) = t$ [L]; $u(s) = q(s)/\phi$ [LT⁻¹]; the integral ω [T²L⁻¹] reflects variations in dispersion resulting from variations in flow velocity field.

The solution of Eq. 1.138 at constant initial and boundary conditions takes the form (1.96), where

$$\xi = \frac{\eta}{\sqrt{4\delta_L\omega}} = \frac{t_0(s) - t}{\sqrt{4\delta_L\omega}}. \quad (1.139)$$

When the solute enters the aquifer as a pulse injection, the concentration function has the form (Welty and Gelhar 1994):

$$C(s, t) = \frac{M}{A_0 \phi u(s_0) \sqrt{4\pi\delta_L\omega}} \exp \left[-\frac{(t_0(s) - t)^2}{4\delta_L\omega} \right], \quad (1.140)$$

where M is the mass of the solute injected in point $s = s_0$, A_0 is the cross-section area of the streamtube, $u(s_0)$ is the real flow velocity in the injection point at the moment $t = 0$.

1.4 Spatial (2D and 3D) Models of Microdispersion in Unidirectional Steady-State Flow

The manifestations of transverse dispersion effects can be exemplified by the analysis of solutions of advection–dispersion equation in a unidirectional (plane-parallel) flow, which in the general three-dimensional case has the form

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} - D_{xx} \frac{\partial^2 C}{\partial x^2} - D_{yy} \frac{\partial^2 C}{\partial y^2} - D_{zz} \frac{\partial^2 C}{\partial z^2} = 0, \quad (1.141)$$

where $D_{xx} = \delta_L u + D_m$ and $D_{yy} = \delta_T u + D_m$, $D_{zz} = \delta_T u + D_m$ are coefficients of longitudinal and transverse (in plan and profile) hydrodynamic dispersion (1.22).

The basic solutions of the formulated problem can be classified, depending on the shape of the solute source, the character of the input concentration signal, and the geometry of the flow domain (flows in unbounded domains or in domains with natural geological boundaries). Moreover, the final analytic relationships can differ, depending on the mathematical methods used to solve the boundary-value problems.

1.4.1 Basic Solutions for a Point Source

These solutions describe the concentration distribution resulting from a pulse (C_i) or a continuous (C) point source in a unidirectional flow field. Given the solution for function C_i with respect to a unit mass of the injected liquid ($M=1$), we can obtain the solution for a point source with a time-varying rate of $P_{ND}(t) = dM(t)/dt$, by using the integral equality

$$C = \int_0^t P_{ND} C'_i(t - \tau) d\tau \quad (1.142)$$

($C'_i = C_i(M=1)$) or for a source with constant rate ($dM/dt = \text{const}$):

$$C = P_{ND} \int_0^t C'_i(t - \tau) d\tau. \quad (1.142a)$$

The subscript ND is the dimensions of the process (2D or 3D).

The solution of the migration problem in a complete three-dimensional formulation for an instantaneous (pulse) point source (Fig. 1.6a), implies that the following initial condition is specified

$$C_i(x, y, z, 0) = \frac{M}{\phi} \delta(x, y, z), \quad (1.143)$$

here $\delta(x, y, z)$ is Dirac delta function [L^{-3}]; ϕ is porosity; M is the total mass of the dissolved species injected into the pore medium in point $x=0$, $y=0$, $z=0$ in moment $t=0$ [M], where

$$M = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C_i(x, y, z) \phi dx dy dz. \quad (1.144)$$

In the context of the mathematical formulation of initial condition (1.143), the source is assumed to have mass but not volume; however, physically, the variable

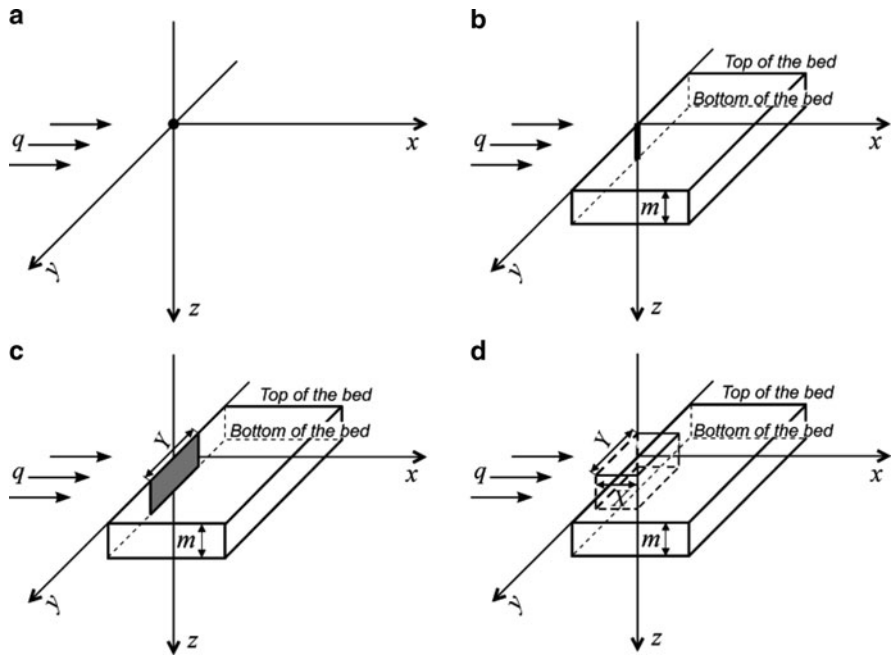


Fig. 1.6 Concentration sources in a unidirectional flow in porous medium. (a) A point source in an unbounded three-dimensional space, (b) a point source with a rate uniformly distributed over the thickness of a bed with top and bottom horizontal boundaries, (c) planar, (d) spatial

M should be associated with the product $C_0 V_0$, where C_0 is the concentration, and V_0 is the volume of the solution that was instantaneously (theoretically, within time $t \rightarrow 0$) injected into the medium.

When the bed boundaries are very far (theoretically, at infinity), the boundary conditions become

$$C_i(\infty, y, z, t) = 0, \quad C_i(x, \infty, z, t) = 0, \quad C_i(x, y, \infty, t) = 0. \quad (1.145)$$

Otherwise, superposition principle is used to take into account the reflecting effect of the boundaries (e.g., impermeable top and bottom) of the bed (Sect. 1.4.6).

An effective method for solving the problems of spatial hydrodynamic dispersion is based on the transformation of the original equations of the type of (1.141) with the use of *Green functions*, G (Galya 1987; Charbeneau 2000; Leij and van Genuchten 2000; Leij et al. 2000; Park and Zhan 2001) followed by integration in the domain x, y, z, t . This type of procedure results in the general solution of Eq. 1.141 in the form

$$C(x, y, z, t) = \int \int \int C(\xi, \eta, \zeta, 0) G_x G_y G_z d\xi d\eta d\zeta, \quad (1.146)$$

where $C(\xi, \eta, \zeta, 0)$ is the initial condition, G_x , G_y and G_z are one-dimensional Green functions, defined for unbounded medium as

$$G_x(x, t, \xi) = \frac{1}{\sqrt{4\pi D_{xx}t}} \exp\left(-\frac{(x-\xi-ut)^2}{4D_{xx}t}\right), \quad (1.147a)$$

$$G_y(y, t, \eta) = \frac{1}{\sqrt{4\pi D_{yy}t}} \exp\left(-\frac{(y-\eta)^2}{4D_{yy}t}\right), \quad (1.147b)$$

$$G_z(z, t, \zeta) = \frac{1}{\sqrt{4\pi D_{zz}t}} \exp\left(-\frac{(z-\zeta)^2}{4D_{zz}t}\right). \quad (1.147c)$$

Green function $G_\zeta(\zeta, t, \zeta')$ for solute transport Eq. 1.141 is the concentration created in point ζ in moment t by a unit-rate ($M = 1$), source concentrated in point ζ' in moment $t = 0$. Green functions in the form (1.147) have been obtained for the conditions: $\partial G_x / \partial \xi = 0$, $\xi \rightarrow \pm\infty$; $\partial G_y / \partial \eta = 0$, $\eta \rightarrow \pm\infty$; $\partial G_z / \partial \zeta = 0$, $\zeta \rightarrow \pm\infty$. Other representations of these functions, taking into account the features of advection–dispersion fluxes at domain boundaries, in particular, on the source contour, can be found, for example, in works (Leij and van Genuchten 2000; Leij et al. 2000; Park and Zhan 2001). The same authors suggest a more general form of solution for Eq. 1.141 with the use of Green functions, including the integration limits, to be specified for concentration sources of fixed (finite) size.

The substitution of condition (1.143) into (1.146) yields the fundamental solution of the problem for a point concentration source, explicitly involving Green function:

$$C_i(x, y, z, t) = \frac{M}{\phi} G_x(x, t) G_y(y, t) G_z(z, t), \quad (1.148)$$

$$G_x(x, t) = \frac{1}{\sqrt{4\pi D_{xx}t}} \exp\left[-\frac{(x-ut)^2}{4D_{xx}t}\right], \quad (1.149a)$$

$$G_y(y, t) = \frac{1}{\sqrt{4\pi D_{yy}t}} \exp\left(-\frac{y^2}{4D_{yy}t}\right), \quad (1.149b)$$

$$G_z(z, t) = \frac{1}{\sqrt{4\pi D_{zz}t}} \exp\left(-\frac{z^2}{4D_{zz}t}\right). \quad (1.149c)$$

The maximal concentration is defined as

$$C_{\max} = C_i(x = ut, 0, 0) = \frac{M}{8\phi\sqrt{\pi^3 D_{xx}D_{yy}D_{zz}t^3}}. \quad (1.150)$$

The solution for a permanently active source can be obtained by integrating solution (1.148) according to (1.142a) (Hunt 1978):

$$C(x, y, z, t) = \frac{1}{M} \frac{dM}{dt} \int_0^t C_i(x, y, z, t - \tau) d\tau = \frac{P_{3D}}{8\pi r \phi \sqrt{D_{yy} D_{zz}}} \left[\exp\left(\frac{x-r}{B}\right) \operatorname{erfc}\left(\frac{2\chi - r/B}{2\sqrt{\chi}}\right) + \exp\left(\frac{x+r}{B}\right) \operatorname{erfc}\left(\frac{2\chi + r/B}{2\sqrt{\chi}}\right) \right], \quad (1.151)$$

where $r = \sqrt{x^2 + \frac{D_{xx}}{D_{yy}} y^2 + \frac{D_{xx}}{D_{zz}} z^2}$, $B = 2D_{xx}/u$, $\chi = \frac{r^2}{4D_{xx}t}$, $P_{3D} = dM/dt$ is mass flux $[\text{MT}^{-1}]$.

1.4.2 Approximate Solutions for 2D and 3D Solute Transport Problems

To analyze the spatial microdispersion in a bed with limited thickness (Fig. 1.6b), of use can be the solution of the problem in two-dimensional planar formulation. The initial condition for an impulse concentration source has the form

$$C_i(x, y, 0) = \frac{M}{\phi m} \delta(x, y), \quad (1.152)$$

where the condition for solute mass balance can be written as

$$M = C_0 V_0 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C_i(x, y) \phi m dx dy \quad (1.152a)$$

(m is the bed thickness $[\text{L}]$; $\delta(x, y)$ is the Dirac delta function $[\text{L}^{-2}]$).

Now the integration of (1.146) yields

$$C_i(x, y, t) = \frac{M}{\phi m} G_x(x, t) G_y(y, t), \quad (1.153)$$

where the Green functions are determined by (1.149a) and (1.149b).

By analogy with (1.146), we have the following representation of the solution of two-dimensional problem in the integral form:

$$\begin{aligned}
C(x, y, t) &= \frac{1}{M} \frac{dM}{dt} \int_0^t C_i(x, y, t - \tau) d\tau \\
&= \frac{P_{2D} \exp\left(\frac{ux}{2D_{xx}}\right)}{4\pi\phi\sqrt{D_{xx}D_{yy}}} \int_0^t \exp\left[-\frac{\frac{x^2}{D_{xx}} + \frac{y^2}{D_{yy}}}{4(t-\tau)} - \frac{u^2(t-\tau)}{4D_{xx}}\right] \frac{d\tau}{t-\tau}, \quad (1.154)
\end{aligned}$$

where $P_{2D} = \frac{1}{M} \frac{dM}{dt}$ is the specific (per unit bed thickness) rate of the concentration source [$\text{ML}^{-1}\text{T}^{-1}$].

As can be seen (Hunt 1978), the integral in solution (1.154) is formally identical to the “leakage function” in the flow problem for a well. Therefore, the solution (1.154) can be written as

$$C(x, y, t) = \frac{P_{2D}}{4\pi\phi\sqrt{D_{xx}D_{yy}}} \exp\left(\frac{x}{B}\right) W\left(\chi, \frac{r}{B}\right), \quad (1.155)$$

where $B = 2D_{xx}/u$, $\chi = \frac{r^2}{4D_{xx}t}$, $r = \sqrt{x^2 + \frac{D_{xx}}{D_{yy}}y^2}$. For an unstable component: (Wilson and Miller 1978) $\chi = r^2/(4dD_{xx}t)$, $r = \sqrt{(x^2 + (D_{xx}/D_{yy})y^2)d}$, $d = 1 + 2\lambda B/u$ (λ is the decay constant). At large r/B , which are of greatest practical interest, function $W(\chi, r/B)$ has the following asymptotic representation (Allen 1985):

$$W(\chi, r/B) \approx \sqrt{\frac{\pi}{2r/B}} \exp\left(-\frac{r}{B}\right) \text{erfc}\left(\frac{2\chi - r/B}{2\sqrt{\chi}}\right). \quad (1.156)$$

The sufficiently high calculation accuracy can be attained at $r/B > 5$ with the additional condition $\chi < r/B$ ($r < 2ut$).

The integration of the basic solutions given here over space coordinates or the direct use of solution (1.146), involving specially defined Green functions, allows solutions to be obtained for concentration sources with different configurations. For example, in the case of a finite-size impulse source located in a vertical plane orthogonal to the flow (planar problem, Fig. 1.6c), we have the solution

$$C_i(x, y, t) = \frac{M}{\phi m} G_x(x, t) Y_0(y, t), \quad (1.157)$$

where

$$G_x(x, t) = \frac{1}{\sqrt{4\pi D_{xx}t}} \exp\left[-\frac{(x-ut)^2}{4D_{xx}t}\right], \quad (1.157a)$$

$$Y_0(y, t) = \frac{1}{2Y} \left[\text{erfc}\left(\frac{y-Y/2}{2\sqrt{D_{yy}t}}\right) - \text{erfc}\left(\frac{y+Y/2}{2\sqrt{D_{yy}t}}\right) \right]; \quad (1.157b)$$

here $Y/2$ is half the source length.

In the case of a spatial source ($X \times Y \times m$) (Fig. 1.6, d), the initial mass of the species can be determined as

$$M = C_0 \phi V_0 = C_0 \phi m X Y, \quad (1.158)$$

where C_0 is the concentration uniformly distributed in volume V_0 .

The solution of a two-dimensional problem, obtained with the use of Green function, has the form (Galya 1987)

$$C_i(x, y, t) = \frac{M}{\phi m} X_0(x, t) Y_0(y, t), \quad (1.159)$$

where

$$X_0(x, t) = \frac{1}{2X} \left[\operatorname{erfc} \left(\frac{x - ut - X/2}{2\sqrt{D_{xx}t}} \right) - \operatorname{erfc} \left(\frac{x - ut + X/2}{2\sqrt{D_{xx}t}} \right) \right], \quad (1.159a)$$

$$Y_0(y, t) = \frac{1}{2Y} \left[\operatorname{erfc} \left(\frac{y - Y/2}{2\sqrt{D_{yy}t}} \right) - \operatorname{erfc} \left(\frac{y + Y/2}{2\sqrt{D_{yy}t}} \right) \right]. \quad (1.159b)$$

The position of the source is defined as $-X/2 \leq x \leq X/2$, $-Y/2 \leq y \leq Y/2$ (an axis of symmetry passes through point $x = 0$, $y = 0$). Substituting (1.159a) and (1.159b) and the expression for mass M into the general solution (1.159), we obtain

$$\begin{aligned} C_i(x, y, t) &= \frac{C_0}{4} \left[\operatorname{erfc} \left(\frac{x - ut - X/2}{2\sqrt{D_{xx}t}} \right) - \operatorname{erfc} \left(\frac{x - ut + X/2}{2\sqrt{D_{xx}t}} \right) \right] \\ &\times \left[\operatorname{erfc} \left(\frac{y - Y/2}{2\sqrt{D_{yy}t}} \right) - \operatorname{erfc} \left(\frac{y + Y/2}{2\sqrt{D_{yy}t}} \right) \right]. \end{aligned} \quad (1.160)$$

It can be easily seen that at large x , y , t , the solution of the problem tends to the above-obtained solutions for point (1.153) or two-dimensional (1.157) sources (see also Sect. 1.4.4).

Integration of solutions (1.157) and (1.160), according to (1.142a) and (1.142), allows us to obtain appropriate solutions for a permanently operating concentration source or sources, whose rate is a function of time (Leij and van Genuchten 2000).

1.4.3 Steady-State Asymptotics

All above solutions for spatial microdispersion in the case of permanently operating sources have steady-state asymptotics for very large time ($t \rightarrow \infty$). They describe the so-called steady-state pollution plumes, within which the concentration of the species does not change over time.

For example, with $t \rightarrow \infty$ solution (1.151) takes the form

$$C(x, y, z, t \rightarrow \infty) = \frac{P_{3D}}{4\pi\phi r\sqrt{D_{yy}D_{zz}}} \exp\left(-\frac{r-x}{B}\right). \quad (1.161)$$

At $D_{xx} \rightarrow 0$ formula (1.161) becomes

$$C = \frac{P_{3D}}{4\pi\phi x\sqrt{D_{yy}D_{zz}}} \exp\left(-\frac{y^2}{4D_{yy}x/u} - \frac{z^2}{4D_{zz}x/u}\right). \quad (1.161a)$$

If we put $D_{yy} = D_{zz} = D_T$, we obtain

$$C = \frac{P_{3D}}{4\pi\phi xD_T} \exp\left(-\frac{y^2 + z^2}{4D_T x/u}\right). \quad (1.162b)$$

Solutions for two-dimensional solute transport also come to similar limiting value (at $t \rightarrow \infty$). In particular, in the solution (1.155) at $\chi = r^2/4D_{xx}t < 1$ (as well as at large $r/B > 5$), we have $W(\chi, r/B) \approx W(0, r/B) = 2K_0(r/B)$, where $K_0(z)$ is modified zero-order Bessel function of the second kind. With Bessel function $K_0(z)$ approximated at $z > 5$ by the relationship

$$K_0(z) \approx \sqrt{\frac{\pi}{2z}} \left(1 - \frac{1}{8z}\right) e^{-z} \approx \sqrt{\frac{\pi}{2z}} e^{-z},$$

the solution (1.155) will be transformed to the steady-state form

$$C(x, y, t \rightarrow \infty) = \frac{P_{2D}}{2\phi\sqrt{\pi D_{yy}ru}} \exp\left(-\frac{r-x}{B}\right), r = \sqrt{x^2 + \frac{D_{xx}}{D_{yy}}y^2}. \quad (1.163)$$

When the transverse dispersion is significant, the contribution of longitudinal dispersion can be neglected and it is worthwhile to extend the solution to the case $D_{xx} \rightarrow 0$:

$$C = \frac{P_{2D}}{2\phi\sqrt{\pi D_{yy}xu}} \exp\left(-\frac{y^2}{4D_{yy}x/u}\right). \quad (1.163a)$$

The solution of the stationary problem of two-dimensional transport from a two-dimensional source orthogonal to flow direction (Fig. 1.6c) takes the form

$$C = \frac{C_0}{2} \left[\operatorname{erfc}\left(\frac{y-Y/2}{2\sqrt{D_{yy}x/u}}\right) - \operatorname{erfc}\left(\frac{y+Y/2}{2\sqrt{D_{yy}x/u}}\right) \right]. \quad (1.164)$$

The asymptotic solution (1.164) can be represented in the form

$$C = \frac{C_0 Y}{2\sqrt{\pi D_{yy} x/u}} \exp\left(-\frac{y^2}{4D_{yy} x/u}\right), \quad (1.164a)$$

similar to relationship (1.163a) for a point source with a strength of $P_{2D} = C_0 q Y$. The condition for the asymptotic (1.164a) to be applicable is $Y^2 u/x D_{yy} < 4 - 8$.

Analyzing the character of the asymptotic distribution of concentration for central axes ($y = 0, z = 0$) of the plumes that form under the effect of sources with constant strength, we note that $C \sim 1/\sqrt{x}$ for two-dimensional dispersion and $C \sim 1/x$ for three-dimensional dispersion, i.e., the spatial gradient of species concentration increases with increasing dimension of the migration flow; in other words, the plume will be localized closer to the source in the case of three-dimensional dispersion. In the case of impulse sources in two-dimensional dispersion problems, $C_{\max} \sim 1/t$, while in the three-dimensional case, $C_{\max} \sim 1/t\sqrt{t}$.

Moreover, the analysis of available solutions for different types of sources (Sagar 1982; Domenico 1987; Alexeev et al. 1989; Charbeneau 2000) shows all of them to yield similar results which do not depend (the values of P_{2D} and P_{3D} being equal) on the shape of the source at large distance from it.

1.4.4 Approximate Solutions for a Finite-Size Source

Suppose that

$$\eta = x - ut, \quad \tau = t \quad (1.165)$$

are linear transformations allowing one to consider process in moving coordinates. By using the chain rule for partial derivatives (see (1.93)), we transform (1.141) into

$$\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \bar{\eta}^2} + \frac{\partial^2 C}{\partial \bar{y}^2} + \frac{\partial^2 C}{\partial \bar{z}^2}, \quad (1.166)$$

where

$$\bar{\eta} = \left(\frac{1}{D_{xx}}\right)^{1/2} (x - ut), \quad \bar{y} = \left(\frac{1}{D_{yy}}\right)^{1/2} y, \quad \bar{z} = \left(\frac{1}{D_{zz}}\right)^{1/2} z. \quad (1.166a)$$

The boundary conditions that reflect the formation of advection–dispersion flow in an unlimited bed from an impulse source $C_0 = M/(\phi XYZ)$ with the shape of a parallelepiped (the position of its center of mass coincides with the origin $x = y = z = 0$) should be written as

$$C(\bar{\eta}, \bar{y}, \bar{z}, \tau = 0) = C_0 \quad \text{for} \quad -\frac{\bar{\eta}_0}{2} \leq \bar{\eta} \leq \frac{\bar{\eta}_0}{2}, -\frac{\bar{y}_0}{2} \leq \bar{y} \leq \frac{\bar{y}_0}{2}, -\frac{\bar{z}_0}{2} \leq \bar{z} \leq \frac{\bar{z}_0}{2}; \quad (1.167a)$$

$$C(\bar{\eta}, \bar{y}, \bar{z}, \tau = 0) = 0 \quad \text{for} \quad |\bar{\eta}| > \frac{\bar{\eta}_0}{2}, |\bar{y}| > \frac{\bar{y}_0}{2}, |\bar{z}| > \frac{\bar{z}_0}{2} \quad (1.167b)$$

$$\left(\text{where } \frac{\bar{\eta}_0}{2} = \left(\frac{1}{D_{xx}} \right)^{1/2} \frac{X}{2}, \frac{\bar{y}_0}{2} = \left(\frac{1}{D_{yy}} \right)^{1/2} \frac{Y}{2}, \frac{\bar{z}_0}{2} = \left(\frac{1}{D_{zz}} \right)^{1/2} \frac{Z}{2} \right); \quad (1.167c)$$

$$C(\bar{\eta}, \bar{y}, \bar{z}, \tau) = 0, (\bar{\eta}^2 + \bar{y}^2 + \bar{z}^2)^{1/2} \rightarrow \infty. \quad (1.167d)$$

The solution of diffusion-type Eq. 1.166 with boundary conditions (1.167) is known (Carslaw and Jaeger 1959; Batu 2006):

$$\begin{aligned} C(\bar{\eta}, \bar{y}, \bar{z}, \tau) = & \frac{C_0}{8} \left[\operatorname{erf} \left(\frac{\bar{\eta}_0/2 - \bar{\eta}}{2\sqrt{\tau}} \right) + \operatorname{erf} \left(\frac{\bar{\eta}_0/2 + \bar{\eta}}{2\sqrt{\tau}} \right) \right] \\ & \times \left[\operatorname{erf} \left(\frac{\bar{y}_0/2 - \bar{y}}{2\sqrt{\tau}} \right) + \operatorname{erf} \left(\frac{\bar{y}_0/2 + \bar{y}}{2\sqrt{\tau}} \right) \right] \\ & \times \left[\operatorname{erf} \left(\frac{\bar{z}_0/2 - \bar{z}}{2\sqrt{\tau}} \right) + \operatorname{erf} \left(\frac{\bar{z}_0/2 + \bar{z}}{2\sqrt{\tau}} \right) \right]. \end{aligned} \quad (1.168)$$

Passing to dimensional variables, we obtain

$$\begin{aligned} \bar{C}(x, y, z, t) = & \frac{1}{8} \left[\operatorname{erfc} \left(\frac{x - ut - X/2}{2\sqrt{D_{xx}t}} \right) - \operatorname{erfc} \left(\frac{x - ut + X/2}{2\sqrt{D_{xx}t}} \right) \right] \\ & \times \left[\operatorname{erfc} \left(\frac{y - Y/2}{2\sqrt{D_{yy}t}} \right) - \operatorname{erfc} \left(\frac{y + Y/2}{2\sqrt{D_{yy}t}} \right) \right] \\ & \times \left[\operatorname{erfc} \left(\frac{z - Z/2}{2\sqrt{D_{zz}t}} \right) - \operatorname{erfc} \left(\frac{z + Z/2}{2\sqrt{D_{zz}t}} \right) \right]. \end{aligned} \quad (1.169)$$

Clearly, solution (1.169) is valid when the characteristic parameter $Pe = ux/D_{xx}$ is large enough. Otherwise, calculation errors will appear because of the problem being solved in a moving coordinate system.

Finally, assuming that variable t in the summands of solution (1.169) that are responsible for the transverse dispersion (the latter two terms in brackets in 1.169) can be changed to the time coordinate x/u corresponding to piston-type replacement, the solution of the problem in question can be written in an approximate form as the product of three functions

$$\bar{C}(x, y, z, t) \approx f_x(x, t) \times f_y(y, x) \times f_z(z, x), \quad (1.170)$$

i.e., the function sought for is the product of particular solutions (f_ξ), including:

- one-dimensional non-steady-state problem of solute transport in the direction of flow in the case of spatially limited input concentration signal, specified in the interval $-X/2 \leq x \leq X/2$ on an infinite axis

$$f_x(x, t) = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{x - ut - X/2}{2\sqrt{D_{xx}t}} \right) - \operatorname{erfc} \left(\frac{x - ut + X/2}{2\sqrt{D_{xx}t}} \right) \right]; \quad (1.171a)$$

- two-dimensional steady-state dispersion problems (in the direction of y and z coordinate axes) from linear sources

$$f_y(y, x) = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{y - Y/2}{2\sqrt{D_{yy}x/u}} \right) - \operatorname{erfc} \left(\frac{y + Y/2}{2\sqrt{D_{yy}x/u}} \right) \right], \quad (1.171b)$$

$$f_z(z, x) = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{z - Z/2}{2\sqrt{D_{zz}x/u}} \right) - \operatorname{erfc} \left(\frac{z + Z/2}{2\sqrt{D_{zz}x/u}} \right) \right]. \quad (1.171c)$$

Formula (1.170) was found to be applicable to the approximate description of the formation of three-dimensional concentration field from a two-dimensional rectangular concentration source (with sides of Y and Z) lying in the plane orthogonal to the flow direction in a bed with unlimited thickness under the assumption that (Domenico and Robbins 1985)

$$f_x(x, t) = \frac{1}{2} \operatorname{erfc} \left(\frac{x - ut}{2\sqrt{D_{xx}t}} \right). \quad (1.172)$$

Clearly, function $f_x(x, t)$ is an approximate solution for the one-dimensional migration problem (see formula 1.96). Formula (1.170) with function $f_x(x, t)$ defined by (1.172) is often referred to as *Domenico's solution*. The approach considered above was later extended to the case of migration of an unstable (decaying) component (Domenico 1987):

$$f_x(x, t) = \frac{1}{2} \exp \left[\frac{ux}{2D_{xx}} \left(1 - \sqrt{1 + \frac{4\lambda D_{xx}}{u^2}} \right) \right] \operatorname{erfc} \left(\frac{x - ut \sqrt{1 + \frac{4\lambda D_{xx}}{u^2}}}{2\sqrt{D_{xx}t}} \right); \quad (1.173)$$

λ is decay constant (see Sect. 1.5.2).

Solution (1.170), which in essence combines one-dimensional solutions to describe the case of three-dimensional dispersion, is one of the most commonly used in this field. At the same time, the solution of the problem in the form (1.170) lacks strict mathematical substantiation (Guyonnet and Neville 2004; West et al. 2007). It is only when the longitudinal dispersivity is very small (theoretically, when $D_{xx} \rightarrow 0$) that the exact (Sect. 1.4.5) and approximate solutions become closer (Srinivasan et al. 2007).

The results of calculations by (1.170) can significantly deviate (with an underestimation of up to several tens of percent) from the exact solution of the corresponding problem in the domains where dispersion processes dominate, i.e., at the periphery of the pollution plume (Guyonnet and Neville 2004; West et al. 2007). The description of the concentration field near the central line of the plume, where advection predominates, does not rule out the use of approximate solution (1.170) with practical purposes (Guyonnet and Neville 2004).

The steady-state asymptotics for solution (1.170) on the central axis ($y, z = 0$) of the plume has the form

$$\begin{aligned} \bar{C}(x, 0, 0, \infty) \\ = \exp \left[\frac{ux}{2D_{xx}} \left(1 - \sqrt{1 + \frac{4\lambda D_{xx}}{u^2}} \right) \right] \operatorname{erf} \left(\frac{Y}{4\sqrt{D_{yy}x/u}} \right) \operatorname{erf} \left(\frac{Z}{4\sqrt{D_{zz}x/u}} \right), \end{aligned} \quad (1.174)$$

where the error function $\operatorname{erf}(\cdot) = 1 - \operatorname{erfc}(\cdot)$.

In the limiting case, where the longitudinal dispersion can be neglected against the background of the intense transverse dispersion, the solutions given above yield time-invariable values of concentrations for the entire domain behind the front of piston-type displacement. Therefore, they can be represented in the equivalent form

$$C(x, y, z, t) = C(y, z, t_0)_{t_0=x/u}, \quad (1.175)$$

thus allowing the concentration at the piston-type displacement front to be calculated for any moment $t = t_0$. For example, in the case considered above (Srinivasan et al. 2007), we have

$$\bar{C}(x, y, z, t) = f_x^0(x, t) \times f_y(y, x) \times f_z(z, x), \quad (1.176)$$

$$f_x^0(x, t) = \begin{cases} 0, & \text{where } t \leq x/u, \\ 1, & \text{where } t > x/u \end{cases} \quad (1.176a)$$

is a step function.

1.4.5 Exact Solutions for 3D Problem

As a reference, we can take the solution (Sagar 1982; Guyonnet and Neville 2004; West et al. 2004)

$$\begin{aligned} \bar{C}(x, y, z, t) = \frac{x \exp(xu/2D_{xx})}{8\sqrt{\pi D_{xx}}} \int_0^t \frac{1}{\tau^{3/2}} \exp \left[- \left(\frac{u^2 \tau}{4D_{xx}} + \frac{x^2}{4D_{xx}\tau} + \lambda \tau \right) \right] \\ \times \left[\operatorname{erfc} \left(\frac{y - Y/2}{2\sqrt{D_{yy}\tau}} \right) - \operatorname{erfc} \left(\frac{y + Y/2}{2\sqrt{D_{yy}\tau}} \right) \right] \\ \times \left[\operatorname{erfc} \left(\frac{z - Z/2}{2\sqrt{D_{zz}\tau}} \right) - \operatorname{erfc} \left(\frac{z + Z/2}{2\sqrt{D_{zz}\tau}} \right) \right] d\tau, \end{aligned} \quad (1.177)$$

which describes the distribution of an unstable component in an unbounded flow in a porous medium (a two-dimensional source). The use of solution (1.177) requires the application of numerical integration.

The change of variable τ to x/u in the arguments of the $\text{erfc}(\cdot)$ functions written in the latter two brackets in (1.177) and accounting for transverse dispersion, allows the solution to be simplified and reduced to Domenico's formula (1.170) at f_ξ , determined by (1.171b), (1.171c) and (1.173) (Srinivasan et al. 2007). As $D_{xx} \rightarrow 0$, solution (1.177) transforms into formula (1.176), where $f_x(x, t) \equiv f_x^0(x, t)$ is the step function (1.176a).

1.4.6 The Influence of Geological Boundaries

So far we have considered beds that have no bounds in either horizontal or vertical direction. The effect of impermeable top and bottom of a bed is accounted for by the superposition method (Bear 1972; Prakash 1982; Park and Zhan 2001). It is based on an infinite number of reflections of image sources located on the z -axis about the top and bottom boundaries of the bed. An acceptable solution of the three-dimensional dispersion problem obtained by using Green function has the form (Park and Zhan 2001):

$$\begin{aligned}
 C(x, y, z, t) = & \frac{1}{4m} \int_0^t Q_v(t - \tau) \exp(-\lambda\tau) \left[\text{erfc} \frac{x - u\tau - x_0}{2\sqrt{D_{xx}\tau}} - \text{erfc} \frac{x - u\tau}{2\sqrt{D_{xx}\tau}} \right] \\
 & \times \left[\text{erfc} \frac{y - y_0}{2\sqrt{D_{yy}\tau}} - \text{erfc} \frac{y + y_0}{2\sqrt{D_{yy}\tau}} \right] \left[z_1 - z_0 + 2 \sum_{k=1}^{\infty} \frac{m}{k\pi} \left(\sin \frac{k\pi z_1}{m} - \sin \frac{k\pi z_0}{m} \right) \right. \\
 & \left. \times \cos \frac{k\pi z}{m} \times \exp \left[- \left(\frac{D_{zz} k^2 \pi^2}{m^2} \right) \tau \right] \right] d\tau,
 \end{aligned} \tag{1.178}$$

where coordinates x_0, y_0, z_0 and z_1 determine the location of the source ($0 \leq x \leq x_0, -y_0 \leq y \leq y_0, z_0 \leq z \leq z_1$), $Q_v(t)$ is the volumetric strength of the source as a function of time [$\text{ML}^{-3}\text{T}^{-1}$], m is bed thickness, λ is decay constant (see Sect. 1.5.2). Solution (1.178) can also be used to describe the concentration field determined by an instantaneous (impulse) source $Q_v(t) = C_0\delta(t)$. For this purpose, $Q_v(t)$ is replaced by C_0 , and no integration is made.

In the simplest case of a point source in the median plane of a bed (Fig. 1.7a), the solution becomes:

$$C' = C(x, y, z, t) + \sum_{k=1}^{\infty} [C(x, y, z - km, t) + C(x, y, z + km, t)], \tag{1.179}$$

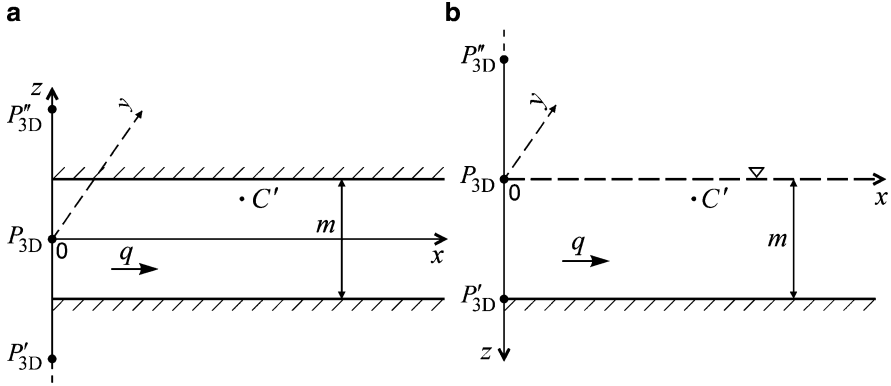


Fig. 1.7 Conceptual diagrams illustrating the derivation of relationships of migration from a point source in beds with limited thickness. (a) A bed with impermeable top and bottom, (b) an unconfined bed

where $C(x, y, z, t)$ is a function of concentration defined by (1.161). From here, we come to the relationship describing the appropriate steady field:

$$C' = \frac{P_{3D}}{4\pi\phi\sqrt{D_{yy}D_{zz}}} \times \left\{ \frac{1}{r} \exp\left(\frac{x-r_k}{B}\right) + \sum_1 \left(\frac{1}{r'} \exp\left(\frac{x-r'}{B}\right) + \frac{1}{r''} \exp\left(\frac{x-r''}{B}\right) \right) \right\}, \quad (1.180)$$

where $r'_k = \sqrt{x^2 + \frac{D_{xx}}{D_{yy}}y^2 + \frac{D_{xx}}{D_{zz}}(z-km)^2}$, $r''_k = \sqrt{x^2 + \frac{D_{xx}}{D_{yy}}y^2 + \frac{D_{xx}}{D_{zz}}(z+km)^2}$.

On the axial line x of the plume at $D_{xx} = 0$:

$$C' = \frac{P_{3D}}{4\pi\eta x\sqrt{D_{yy}D_{zz}}} \left[1 + 2 \sum_1^\infty e^{-(\xi k)^2} \right], \quad (1.181)$$

where $\xi = \sqrt{m^2 u / 4D_{zz}x}$. When $\xi > 2$, the second term in solution (1.181) can be neglected with an error of no more than 4%, and the obtained result becomes identical to the appropriate solution for an unbounded bed (see formula (1.161a) $z = y = 0$).

Another approximation of formula (1.181) can be derived at small ξ . With this in view, let us consider the representation of the sum of the series in (1.181) in the form

$$\sum_1^\infty e^{-(\xi k)^2} = -\frac{1}{2} + \frac{\sqrt{\pi}}{\xi} \left(\frac{1}{2} + \sum_1^\infty e^{-(\pi k/\xi)^2} \right).$$

When $\xi < 1.5$, formula (1.181) transforms, with an error of the same order, into the expression

$$C' = \frac{P_{3D}}{2\phi m \sqrt{\pi D_{yy} x u}}, \quad (1.182)$$

coinciding with the solution of problem (1.163a) of two-dimensional dispersion in $x - y$ domain from a source with a strength of P_{2D} . In other words, when $\xi < 1.5$, the three-dimensional migration problem can be considered in the two-dimensional (in this case, horizontal) formulation, reducing the dimensions of the initial model.

The order of the estimates given here extends to other calculation points not too far from the central line of the plume. These estimates are also true for a source on the surface of an unconfined groundwater flow (Fig. 1.7, b) with m replaced by $2m$.

1.5 Equations for Simplest Chemical Reactions and Transformations

The most significant among such interactions are sorption and decay (destruction) of the migrating constituents, which are commonly included in major solute transport calculation schemes (models) during the solution of hydrogeological problems. The manifestation features of such processes under specific migration conditions (schemes) are discussed in sufficient detail in subsequent sections of this book. Here we will restrict ourselves to the general principles of their physico-mathematical description as applied to solute advection problems in homogeneous media.

1.5.1 Sorption

Assume that the migrating component is instantaneously (*in an equilibrium mode*) sorbed (adsorbed) by aquifer material, following the generalized isothermal relationship:

$$N = f(C). \quad (1.183)$$

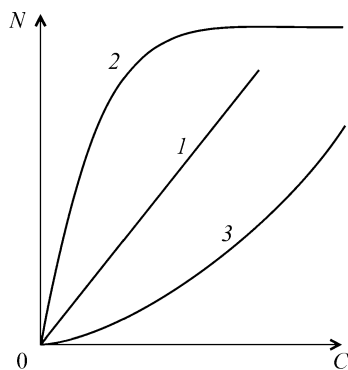
Formula (1.183) demonstrates the relationship between species concentration N on the aquifer material (per unit of the fluid-saturated matrix volume $[\text{ML}^{-3}]$) and its concentration C in the liquid phase $[\text{ML}^{-3}]$, which fills the pore (fracture) space. The plot below (Fig. 1.8) demonstrates three main (typical) shapes of sorption isotherms: linear, convex, and concave.

Now the sorption rate W_s of components from solution is linearly related with the variation rate of mass flux in pores (fractures):

$$W_s = \frac{\partial N}{\partial t} = f'(C) \frac{\partial C}{\partial t}, \quad (1.184)$$

where $f'(C) = \frac{d}{dC}f(C)$ is the derivative of the sorption isotherm with respect to concentration C in solution, calculated at the value C in equilibrium with N .

Fig. 1.8 Typical shapes of sorption isotherms $N = f(C)$. (1) linear, (2) convex, and (3) concave



Substituting (1.184) into the general advective transport equation (1.12, $W_f = 0$) eliminates variable W_s :

$$\tilde{R}(C) \frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C = 0, \quad (1.185)$$

$$\tilde{R}(C) = 1 + \frac{f'(C)}{\phi}, \quad (1.185a)$$

where $\tilde{R}(C)$ is an effective parameter, accounting for an increase in the system capacity due to sorption processes. Similar transformations can be made in the general advection–dispersion equation (see Sect. 1.1.2.5).

In the particular case of *linear isotherm*

$$N = K_d \rho_b C, \quad (1.186)$$

$$\tilde{R}(C) \equiv R \equiv 1 + \frac{K_d \rho_b}{\phi}. \quad (1.187)$$

Relationships (1.186) and (1.187) are written for the conditions of migration in porous medium, where parameter K_d serves as a weight coefficient of sorption distribution [$L^3 M^{-1}$], ρ_b is the bulk dry density of the sediment/soil [ML^{-3}].

In fractured rock, we have $N = K_a S_b C$, and, accordingly,

$$R = 1 + \frac{K_a S_b}{\phi}, \quad (1.187b)$$

where K_a is the surface sorption coefficient of the fracture system [L]; this parameter represents the partitioning between the amount of sorbed concentration of solute per unit surface and the amount of aqueous concentration; S_b is the specific surface area which is defined as the ratio of the fracture surface area to the volume of mobile water in the fracture [L^{-1}].

Coefficient R was called the *retardation (retention) factor*; physically, it is the ratio of water particle motion velocity u in pores or fractures to the transfer velocity u^s of the component being sorbed ($R = u/u^s$).

Thus, in the case of $f' = \text{const}$, Eq. 1.185 is linear and the form of its solutions does not differ from those considered earlier (Sect. 1.2). For example, the solution (1.185) of Cauchy problem in one-dimensional case can be written in the explicit form

$$C = \varphi \left(x - \frac{ut}{R} \right), \quad (1.188)$$

describing a moving wave with constant profile; here, function φ characterizes the initial distribution.

Let us consider in more detail the solution of the base Eq. 1.185 for the general case of *nonlinear isotherm*, when the “effective retardation factor” (1.185a) of the system depends on the concentration function. To simplify the analysis, without loss of generality, we can consider one-dimensional transfer described by the equation

$$\frac{\partial C}{\partial t} + u(C) \frac{\partial C}{\partial x} = 0, \quad (1.189)$$

$$u(C) \equiv u_x(C) = \frac{u_x}{1 + f'(C)/\phi}. \quad (1.189a)$$

Clearly, the migration velocity u of points of the initial concentration wave depends on the shape of the sorption isotherm. For example, it can be easily shown that, in the case of a convex sorption isotherm, the larger the concentration, the faster the motion of the corresponding points of the concentration profile, i.e., $u(C)$ is an increasing function ($u'(C) > 0$).

The solution $C = C(x, t)$ of Cauchy problem for Eq. 1.189 with the initial condition

$$C = \varphi(x) \quad \text{at} \quad t = 0 \quad (-\infty < x < \infty) \quad (1.190)$$

can be represented in the parametric form (Polyanin et al. 2002):

$$x = \xi + U(\xi)t, \quad C = \varphi(\xi), \quad (1.191)$$

where $U(\xi) = u(\varphi(\xi))$.

Let us consider the characteristic straight lines $x = \xi + U(\xi)t$ in the plane x, t at different values of parameter ξ . The slope of these curves is determined by coefficient $U(\xi)$. The concentration is constant along any such line and equal to $C = \varphi(\xi)$. The dependence $u = u(C)$ results in a typical nonlinear effect – a distortion of the profile of the propagating wave.

For definiteness, let us assume $u'(C) > 0$. As it was mentioned above, larger C concentrations propagate with velocities higher than smaller concentrations. If the initial concentration profile at any x satisfies the condition $\varphi'(x) > 0$ (Fig. 1.9a), the characteristics on the x, t plane that issue from points on the x axis into the domain $t > 0$ are diverging straight lines, resulting in the formation of the so-called rarefaction waves (Fig. 1.9c).

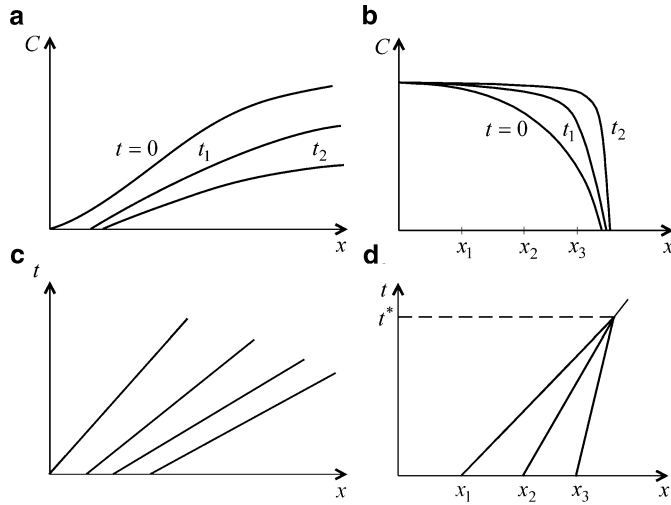


Fig. 1.9 Two types of initial concentration distributions (a) $\varphi'(x) > 0$ and (b) $\varphi'(x) < 0$ and the associated plots of characteristic lines (c) $\varphi'(x) > 0$, (d) $\varphi'(x) < 0$. $u'(C) > 0$

Let us consider another case: $\varphi'(x) < 0$ (Fig. 1.9b). Suppose that x_1 and x_2 are arbitrary points on the abscissa, such that when $x_1 < x_2$, we have $u(x_1) > u(x_2)$. From the first relationship (1.191) it follows that the characteristics issuing from points x_1 and x_2 will intersect (Fig. 1.9d) at the moment

$$t^* = \frac{x_2 - x_1}{u(C_1) - u(C_2)}, \quad (1.192)$$

where $C_1 = \varphi(x_1)$, $C_2 = \varphi(x_2)$. Since the values of C on these characteristics are different, the solution cannot be continuously extended to $t > t^*$.

Clearly, the picture will be inverse when $u'(C) < 0$ and a discontinuity front will form when $\varphi'(x) > 0$.

The further construction of solution requires the replacement of the many-valued part of the concentration profile by an appropriate discontinuity (concentration jump). Suppose that function $C(x, t)$ is discontinuous along line $x = s(t)$ in the plane x, t . Function $C(x, t)$ is smooth and single-valued on either side of the discontinuity and can be described by parametric Eqs. 1.191. Discontinuity propagation velocity $u^* = (dx/dt)_c$ is defined by the expression (Whitham 1974)

$$u^* = \frac{\tilde{u}(C_2) - \tilde{u}(C_1)}{C_2 - C_1}, \quad \tilde{u}(C) = \int u(C) dC, \quad (1.193)$$

following from the mass conservation equation on the moving discontinuity; here, subscripts 1 and 2 correspond to the values before and after the discontinuity, respectively; clearly, $\tilde{u}(C)$ serves as a mass flux.

Let us consider Cauchy problem with a discontinuous initial condition, reflecting the existence of a contrast interface between the displacing liquid and that being displaced:

$$C(x, 0) = \begin{cases} C_1 & \text{for } x < 0, \\ C_2 & \text{for } x > 0. \end{cases} \quad (1.194)$$

Suppose that $u'(C) > 0$ (a convex isotherm).

The generalized solution at $C_1 < C_2$ has the form

$$C(x, t) = \begin{cases} C_1 & \text{at } x/t < u_1^*, \\ u^{-1}(x/t) & \text{at } u_1^* \leq x/t \leq u_2^*, \\ C_2 & \text{at } x/t > u_2^*, \end{cases} \quad (1.195)$$

where $u_1^* = u(C_1)$, $u_2^* = u(C_2)$, u^{-1} is the inverse function to u , i.e., $u^{-1}(u(C)) = C$. This solution is continuous in the domain $t > 0$ and describes a “rarefaction wave”.

The generalized solution at $C_1 > C_2$:

$$C(x, t) = \begin{cases} C_1 & \text{at } x/t < u^*, \\ C_2 & \text{at } x/t > u^*, \end{cases} \quad (1.196)$$

where

$$u^* = \frac{1}{C_2 - C_1} \int_{C_1}^{C_2} u(C) dC, \quad (1.196a)$$

i.e., the solution has a discontinuity on the line $x = u^*t$ and describes the propagation of a “shock wave”.

Dispersion effects cause some changes in the description of concentration fronts subject to the effect of nonlinear sorption (see Sect. 20.1.2).

1.5.2 Decay

The classical representative of the decay process is the *first-order decay* of radionuclides. Many chemical and biological transformations can also be described approximately in terms of first-order decay. The simplest case corresponds to a reaction when a parent component decays to a stable daughter component. Very often however decay proceeds in sequences, degrading the original substance via several intermediates to a final product. That is so called *chain member decay*.

1.5.2.1 Solute Transport Accompanied by One-Step First-Order Decay

The kinetics of one-step decay of a species can be described by the expression

$$W_s \equiv W_s^\lambda = \phi \lambda C, \quad (1.197)$$

introducing linear relationship between the decay rate (W_s^λ) and the residual concentration of the species (C) in the liquid phase; here λ is the decay (destruction) constant [T^{-1}]. Under static (batch) conditions $W_s^\lambda = -\phi \frac{\partial C}{\partial t} = \phi \lambda C$.

Now the general Eq. 1.12, describing three-dimensional migration process (without dispersion and at $W_f = 0$), takes the form

$$\frac{\partial C}{\partial t} + u_x \frac{\partial C}{\partial x} + u_y \frac{\partial C}{\partial y} + u_z \frac{\partial C}{\partial z} = -\lambda C. \quad (1.198)$$

If the characteristic system

$$\frac{dt}{1} = \frac{dx}{u_x} = \frac{dy}{u_y} = \frac{dz}{u_z} = -\frac{dC}{\lambda C}, \quad (1.198a)$$

which is an equivalent form of the linear partial differential Eq. 1.198 has four independent integrals

$$w_i(x, y, z, t, C) = c_i \quad (i = 1, 2, 3, 4), \quad (1.199)$$

then the general solution of Eq. 1.199 can be written as

$$\Phi(w_1, w_2, w_3, w_4) = 0, \quad (1.200)$$

where ϕ is an arbitrary function, c_i is an integration constant.

Since the last integral in the system of Eqs. 1.198a can be written as $Ce^{\lambda t} = c_4$, the solution (1.200) can be represented explicitly as

$$C = e^{-\lambda t} \Psi(w_1, w_2, w_3), \quad (1.201)$$

where Ψ is an arbitrary function.

As an example, consider migration in a one-dimensional flow, which can be described by the equation

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = -\lambda C \quad (u = u_x = \text{const}). \quad (1.202)$$

The integral balance for the characteristic system

$$\frac{dt}{1} = \frac{dx}{u} = -\frac{dC}{\lambda C} \quad (1.203)$$

can be represented in two forms

$$x - ut = c_1 \quad Ce^{\lambda t} = c_2; \quad (1.204a)$$

$$x - ut = c_1 \quad Ce^{\lambda x/u} = c_2. \quad (1.204b)$$

They can be used for solving Cauchy problem in two main formulations (variants), describing the development of the migration process over space and time. In this case, the initial conditions for the problem are formulated either as

$$t = 0, \quad C = \varphi_1(x), \quad (1.205a)$$

when the initial concentration distribution in the flow is known, or as

$$x = 0, \quad C = \varphi_2(t), \quad (1.205b)$$

when the concentration at the inlet section is specified as a function of time.

To solve the problem, let us rewrite the initial conditions (1.205) in the parametric form:

$$t = 0, \quad x = \xi, \quad C = \varphi_1(\xi), \quad (1.206a)$$

$$x = 0, \quad t = \tau, \quad C = \varphi_2(\tau). \quad (1.206b)$$

Let us substitute the initial conditions (1.206) into the respective integrals (1.204) of the characteristic system (1.203). Such substitution yields the constants

$$c_1 = \xi, \quad c_2 = \varphi_1(\xi);$$

$$c_1 = -u\tau, \quad c_2 = \varphi_2(\tau),$$

which can be substituted into Eqs. 1.204 to yield

$$\xi = x - ut, \quad C e^{\lambda t} = \varphi_1(\xi); \quad (1.207a)$$

$$\tau = t - x/u, \quad C e^{\lambda x/u} = \varphi_2(\tau). \quad (1.207b)$$

Thus, the solution of the Cauchy problem for the two variants of initial conditions has the form

$$C = e^{-\lambda t} \varphi_1(x - ut), \quad (1.208a)$$

$$C = e^{-\lambda x/u} \varphi_2(t - x/u). \quad (1.208b)$$

Physically, the obtained results can be interpreted as follows. The solution (1.208a) shows (Fig. 1.10a) that the target concentration in point x at time $t > 0$ is determined by the concentration in point $x - ut$ at the initial moment, multiplied by the exponential term $e^{-\lambda t}$. The solution (1.208b) shows (Fig. 1.10b) that the calculated concentration C in moment t is determined by the value of input concentration function $C(0, t)$ in the moment $t - x/u$, with a correction by exponential factor $e^{-\lambda x/u}$.

With the step concentration function

$$\varphi_1(x) = \begin{cases} C_0 & \text{at } x \leq 0, \\ 0 & \text{at } x > 0, \end{cases} \quad (1.209)$$

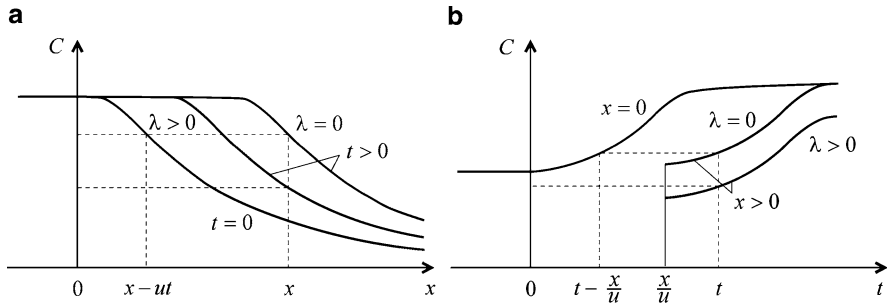


Fig. 1.10 Formation of the concentration profile and breakthrough curves for uneven initial distributions. (a) $C(x, t = 0) = \varphi_1(x)$, (b) $C(x = 0, t) = \varphi_2(t)$

the obtained solution becomes

$$C = \begin{cases} C_0 e^{-\lambda t} & \text{at } t \geq \frac{x}{u}, \\ C_0 e^{-\lambda x/u} & \text{at } x < ut. \end{cases} \quad (1.210)$$

An approximate solution of the one-dimensional advection–dispersion equation with decay

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} - D_L \frac{\partial^2 C}{\partial x^2} = \lambda C \quad (1.211)$$

can be obtained after its transformation into the “diffusion” form

$$\frac{\partial G}{\partial \tau} - D_L \frac{\partial^2 G}{\partial \eta^2} = 0, \quad (1.212)$$

by transforming coordinates in accordance with (1.93) with the change of variable $G = C e^{\lambda t}$. The solution of this equation and the passage to concentration yields the expression

$$\bar{C} = \frac{1}{2} e^{-\lambda t} \operatorname{erfc} \left(\frac{x - ut}{\sqrt{4D_L t}} \right). \quad (1.213)$$

However, due to the physical formulation of the problem, where the process is considered in the unbounded interval $-\infty \leq x \leq \infty$, formula (1.213) is valid only in the case of a decaying source, the concentration in which decreases over time (nonrenewable pollution), according to the same exponential law.

In the general case with a Dirichlet condition on the inlet flow boundary, the problem can be solved by the operator method. In terms of Laplace transforms, the solution has the form similar to (1.113)

$$\bar{C} = \frac{C_0}{p} \exp \left(\frac{ux}{2D_L} \right) \exp \left(-\frac{ux}{2D_L} \sqrt{1 + \frac{4D_L}{u^2} (\lambda + p)} \right). \quad (1.214)$$

The inversion of (1.214) into the real domain yields the following solution (Ogata 1970; van Genuchten 1981):

$$\bar{C} = \frac{1}{2} \exp \left[\frac{x(u - \mu)}{2D_L} \right] \operatorname{erfc} \left(\frac{x - \mu t}{2\sqrt{D_L t}} \right) + \frac{1}{2} \exp \left[\frac{x(u + \mu)}{2D_L} \right] \operatorname{erfc} \left(\frac{x + \mu t}{2\sqrt{D_L t}} \right), \quad (1.215)$$

where $\mu = \sqrt{u^2 + 4\lambda D_L}$. When $\lambda D_L / u^2 < 0.05$, the effect of dispersion can be neglected, allowing one to use relationships given above. As $t \rightarrow \infty$, the solution (1.215) has a steady asymptotics:

$$\bar{C} = \exp \left[\frac{x(u - \mu)}{2D_L} \right]. \quad (1.216)$$

1.5.2.2 Transport of a Decay Chain in Porous Media

A general solution of the problem can be found in Laplace transform (Bauer et al. 2001). Let us assume that a multi-species decay chain is described by the system of differential equations:

$$\begin{aligned} R_1 \frac{\partial C_1}{\partial t} + \nabla \cdot (C_1 \mathbf{u} - \mathbf{D} \cdot \nabla C_1) &= -R_1 \lambda_1 C_1, \\ R_i \frac{\partial C_i}{\partial t} + \nabla \cdot (C_i \mathbf{u} - \mathbf{D} \cdot \nabla C_i) &= -R_i \lambda_i C_i + R_{i-1} \lambda_{i-1} C_{i-1}, \quad i = 2, \dots, N, \end{aligned} \quad (1.217)$$

where C_i is the concentration of the i th element (component) of the decay chain, which comprises N unstable components (i and $i - 1$ are the daughter and parent components, respectively); R_i is the retardation factor for the i th component, defined as $R_i = 1 + \rho_b K_{di} / \phi$; $\mathbf{u} = \mathbf{q} / \phi$. The differential operator and the tensors in (1.217) are defined as in Eq. 1.25.

In terms of Laplace transforms (1.107), system of Eqs. 1.217 takes the form:

$$\begin{aligned} \nabla \cdot (\tilde{C}_1 \mathbf{u} - \mathbf{D} \cdot \nabla \tilde{C}_1) &= -R_1(p + \lambda_1) \tilde{C}_1, \\ \nabla \cdot (\tilde{C}_i \mathbf{u} - \mathbf{D} \cdot \nabla \tilde{C}_i) &= -R_i(p + \lambda_i) \tilde{C}_i + R_{i-1} \lambda_{i-1} \tilde{C}_{i-1}, \quad i = 2, \dots, N. \end{aligned} \quad (1.218)$$

Now a good idea (Bauer et al. 2001) is to write the solution of the system as

$$\tilde{C}_i = \sum_{j=1}^i A_j^i(p) \hat{C}_j(p), \quad (1.219)$$

i.e., as a linear combination of fundamental (basic) solutions $\hat{C}_j(p)$ for $j = 1, \dots, i$, which are defined as solutions of the equations

$$\nabla \cdot (\hat{C}_i(p) \mathbf{u} - \mathbf{D} \cdot \nabla \hat{C}_i(p)) = -R_i(p + \lambda_i) \hat{C}_i, \quad i = 1, \dots, N. \quad (1.220)$$

The fundamental solutions $\hat{C}_i(p)$ are solutions to the transport problem with the decay parameter of each component independent of those of other components of the chain. These solutions are assumed to be known. Now, substituting (1.219) into (1.218) yields an explicit solution for concentration distributions in terms of images. Moreover, it can be shown that the coefficient $A_j^i(p)$ can be uniquely determined from the recurrent equality (Bauer et al. 2001):

$$A_j^i(p) = \frac{R_{i-1} \lambda_{i-1}}{R_i(p + \lambda_i) - R_j(p + \lambda_j)} A_j^{i-1}(p), \quad j < i \quad (1.221)$$

(the combination of parameters R_i and λ_i supposes that $R_i(p + \lambda_i) - R_j(p + \lambda_j) \neq 0$). These transformations are valid for a point source. To pass to the functioning conditions of species sources with a spatial distribution, one needs to modify (1.221).

Thus, to solve the problem, one needs to (1) determine the basic solutions $\hat{C}_i(p)$ for the given flow geometry; (2) to determine the unknown coefficient $A_i^i(p)$, depending on the boundary condition; other coefficients are determined by recurrent formula (1.221); (3) to pass from the domain of transforms with p parameter into the domain of real time t .

For example, with a Dirichlet boundary condition, in the case of one-dimensional linear migration, when $C = C(x, t)$, we have for the two forms of inlet function (see Sect. 1.3.3):

- for constant concentration $C_i(0, t) = C_{0i}$:

$$A_i^i(p) = \frac{C_{0i}}{p} - \sum_{j=1}^{i-1} A_j^i(p), \quad (1.222a)$$

- for impulse function $C_i(0, t) = (M_i/uR_iS)\delta(t)$:

$$A_i^i(p) = \frac{M_i}{uR_iS} - \sum_{j=1}^{i-1} A_j^i(p). \quad (1.222b)$$

It can be shown (Bauer et al. 2001), that in this case, all solutions for $\tilde{C}_i$ can be written as linear combinations of partial solutions in terms of transforms

$$\tilde{f}_1 = \exp\left(\frac{ux}{2D_L} \sqrt{1 + \frac{4D_L}{u^2} R_i(\lambda_i + p)}\right), \quad (1.223a)$$

$$\tilde{f}_2 = \frac{1}{p} \exp\left(\frac{ux}{2D_L} \sqrt{1 + \frac{4D_L}{u^2} R_i(\lambda_i + p)}\right), \quad (1.223b)$$

whose originals are known:

$$f_1 = \frac{x}{t\sqrt{4\pi D_L t/R_i}} \exp\left(-\frac{x^2}{4D_L t/R_i} - \frac{u^2 t}{4R_i D_L} - \lambda_i t\right), \quad (1.224a)$$

$$f_2 = \frac{1}{2} \exp\left[-\frac{x\mu}{2D_L}\right] \operatorname{erfc}\left(\frac{x-\mu t}{2\sqrt{D_L t}}\right) + \frac{1}{2} \exp\left[\frac{x\mu}{2D_L}\right] \operatorname{erfc}\left(\frac{x+\mu t}{2\sqrt{D_L t}}\right), \quad (1.224b)$$

where μ is defined in the same manner as in solution (1.215), describing single-step decay, but with λ replaced by λ_i .

From the analysis given in this chapter one can conclude about a very wide variety of classical Fickian advection–dispersion model applications to study contaminant transport in groundwater. At the same time there are a number of examples showing that the model to be inadequate in simulating field-scale solute transport under certain hydrogeological conditions (Feehley et al. 2000). Thus, the Fickian advection–dispersion approach has severe limitations when applied to highly heterogeneous aquifers with potentials for preferential pathways. The other limitation is associated with the model inability to describe transport in structural rocks with dual porosity/dual permeability. We will focus on these aspects of the solute transport model analysis and development in the following chapters of the present book.

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Chapter 2

Water Movement and Solute Transport in Unsaturated Porous Media

The unsaturated zone, also termed the vadose zone, is the portion of the subsurface above the groundwater table. It contains air as well as water in the pores. This zone is also high in organic matter and clay, which promotes sorption, biological degradation and transformation of contaminants. In industrial or agricultural areas, where the ground surface is contaminated by hazardous wastes or fertilizers and pesticides, the unsaturated zone may be thought of as a buffer zone, which provides protection to the underlying aquifers. Unsaturated zone is often regarded as a filter removing undesirable substances before they affect aquifers, and the hydrogeologic properties of unsaturated zone are the most important factor for groundwater deterioration induced by surface contamination (Stephens 1996; Selker et al. 1999).

On the other hand, from hydrologic viewpoints, unsaturated zone is a zone that to a large degree controls the transmission of water to aquifers, as well as to the land surface, to water on the surface, and to the atmosphere. Processes in the unsaturated zone may be a controlling factor in the distribution of the atmospheric precipitation between runoff, infiltration, and evapotranspiration.

Therefore the knowledge and understanding of water flow and solute transport in the unsaturated zone is becoming increasingly important especially in terms of water resources planning and management, water quality management and the mitigation of groundwater pollution. The presence of different phases (soil/sediment matrix, water and air) results in many different physical and chemical processes taking place. These processes are often complex and require simplifying assumptions to provide achievable and verifiable results in terms of water and solute solution profiles in the shallow sediments (Selker et al. 1999; Gandola et al. 2001).

The assessment of groundwater protection against pollution requires the joint consideration of the processes of moisture and solute transfer under incomplete saturation. The rate of flow (infiltration) and the distribution of moisture in the vertical profile are functions (often nonstationary), the knowledge of which is a prerequisite for the correct solution of mass transfer problems. Strictly speaking, the presence of air in the subsurface material as an independent phase requires the consideration of multiphase flow models (Bear and Cheng 2010). The behavior of the system in the case of multiphase flow is governed by the relationship between capillary pressure P^c , volumetric water content θ (or saturation S), and the hydraulic conductivity k : $P^c - \theta - k$, which is referred to as the basic relationship.

However, the formulation and solution of many problems can be simplified, if only the motion of the liquid phase is considered, with the assumption that ideal (without resistance) counterflow of pore air exists, such that its pressure in any point is always constant and equal to the atmospheric pressure, both within the wetting zone and between the infiltration front and groundwater table. Therefore, hereafter we will consider only two migration “components”: the moisture and the solute. The presence of air will be accounted for indirectly through the transfer coefficient and storage characteristics.

Quantification of flow and transport in unsaturated *fractured rocks* requires often conceptualizing these processes in terms of discrete fracture network (DFN) or stochastic fracture-continuum (SFC) models (Neuman 2005). The DFN approach considers random networks as interconnected line or plane segments embedded in a low permeable matrix. SFC approach conceptualizes heterogeneous fracture media with a stochastic spatial distribution of fracture permeability and geometric parameters. Theoretical analysis and numerical modeling show discrete features of flow paths in individual fractures: overall gravity driven flow in the fracture network may focus in a few paths. Similar to sub-horizontal flow in aquifers (Sect. 1.1.1) the flux that occurs in the system of focused flow paths can be up to ten times more than the areally distributed infiltration flux prescribed at the inflow boundary (Pruess 1999; Liu et al. 2002; Zhang et al. 2004). It means that water can flow rapidly through fracture networks along localized preferential pathways, moreover under the natural conditions most such seepage may proceed in an unsteady and episodic manner. The mentioned phenomena are subject of special investigations related to development of sophisticated models of fracture networks based on statistical information derived from field-measured fracture data.

This chapter reviews only the fundamental mechanisms governing flow and transport in unsaturated zone represented by homogeneous single porosity shallow sediments employing macroscale continuum concept. An important attribute of the subsurface transport models is the link between fracture surface and matrix processes unified by the matrix potential (Chap. 7).

2.1 Basic Soil-Water Movement and Infiltration Models

Models for wetting-front migration and water saturation distribution behind the front provide the basis for mass-conservative coupling of fluid flow and solute transport in soils and unsaturated geological media. The main focus is detailed analysis of typical one-dimensional infiltration problems formulated here for the use in a further study of transport phenomena in homogeneous environment, ignoring the soil heterogeneity and preferential flow (Sect. 2.2). Also, the models discussed in this chapter can potentially be expanded to studying solute transfer processes in the unsaturated zone represented by structured soils with macropores or fractured formations exhibiting a dual porosity behavior (Chap. 7).

2.1.1 Governing Functions and Parameters

2.1.1.1 Soil Water Potential

The total status of energy for water in partially saturated porous material is described by the total moisture potential (Nielsen 1991; Weight 2008), φ_t ,

$$\varphi_t = \varphi_g + \varphi_m, \quad (2.1)$$

where $\varphi_g = gz$ and $\varphi_m = P/\rho_w$ are the gravitational and matrix (or soil water) potentials [L^2T^{-2}], g is the acceleration due to gravity [LT^{-2}], $z > 0$ is the elevation above an arbitrary datum [L], ρ_w is water density [ML^{-3}], P is the hydrostatic pressure [$ML^{-1}T^{-2}$]. The gravitational potential presents a potential energy due to the vertical location of the liquid in the elementary volume of the unsaturated porous media. The matrix potential is an integral characteristic of the manifestation of capillary-adsorption forces caused by the presence of interphase boundaries in the pore space (the rock matrix, the water and air phases).

The total potential, φ_t , in the vadose zone can be converted to hydraulic (or piezometric) head (as is typically made in subsurface hydrology) by dividing by the acceleration due to gravity:

$$h = z + \psi, \quad (2.2)$$

where ψ is the *pore water (capillary) pressure head* [L]. Thus, the hydraulic head is the sum of the pressure head, $\psi = P/\rho_w g \leq 0$, and the position, z (the z -axis is directed vertically upward). If the air forms a continuous phase, the hydrostatic pressure in water (P_w) is less than the pressure in the air (P_g). In this case, the pressure P , reduced to the atmospheric pressure is $P_w - P_g < 0$, therefore, the pressure head

$$\psi = \frac{P}{\rho_w g} \equiv -\frac{P^c}{\rho_w g} \quad (2.3)$$

(P^c is the capillary pressure) is also negative. Function ψ characterizes the work against the capillary-adsorption forces performed to withdraw water from unsaturated porous medium and hence is a potential characteristic. Considering that saturation at the phreatic water surface is complete and $\psi = 0$, we have $h = z$.

Moisture transport in the aeration zone is largely determined by the functional relationship between its three major characteristics

$$\psi - \theta - k.$$

This relationship, which is commonly nonlinear, largely determines the specific approach to be used to solve the equations describing the migration of water and chemicals dissolved in it in the aeration zone represented by unconsolidated sedimentary materials (often referred to as soil) and rocks.

2.1.1.2 Water Retention Curves

Pressure head is a function of the moisture content of subsurface materials, θ : $\psi = f(\theta)$. This function is referred to as the *water retention curve*, and is also called the *soil moisture characteristic*. The empirical expressions fitted to data of physical experiments and relating the characteristics ψ and θ are very diverse. Thus, the shape of water retention curves can be characterized by several models. The relationships of the form

$$\psi = f(\theta) \text{ or } \theta = f^{-1}(\psi) \quad (2.4)$$

are commonly nonlinear.

The simplest one is the exponential function of the form:

$$\bar{\theta}(\psi) = e^{\alpha\psi} (\psi \leq 0), \bar{\theta} = \frac{\theta - \theta_r}{\theta_s - \theta_r}, \quad (2.5)$$

where $\bar{\theta}$ is the normalized volumetric water content, θ_s is the saturated volumetric water content (maximum water content), θ_r is the residual volumetric water content, α is the sorptive number, regarded as the reciprocal of the capillary length scale [L^{-1}], $\alpha \sim 1/h_c$ (h_c is an adduced capillary height). Sometimes this coefficient is called the desaturation coefficient which represents the desaturation rate of the soil-water characteristic curve (Ng and Menzies 2007); the value α is related to the soil grain size distribution.

With respect to the applicability of Eq. 2.5, it should be noted: (1) the relative degree of water saturation (effective water saturation), $\bar{S}$, which indicates the percentage of the voids filled with water, is often used in place of the normalized water content, $\bar{\theta}$; (2) the difference between the saturated soil water content and the residual soil water content $\Delta\theta = \theta_s - \theta_r$ in (2.5) is called *soil moisture capacity*; (3) for the subsequent expert estimates, the parameter α may be assumed to vary within the most likely range from 0.5 (clays and loams) to 10 m^{-1} (sand type of sediments), thus, the greater the clay content, the smaller the value of α . The relationship (2.5), which has been thoroughly studied before (Gardner 1958), is often referred to as the *Gardner formula* in the scientific literature.

Widely used in the practice is the exponential *Brook–Corey function* (Brooks and Corey 1964; Corey 1977):

$$\bar{\theta}(\psi) = \begin{cases} \left(\frac{\psi_d}{\psi} \right)^\lambda & \psi < \psi_d, \\ 1 & \psi \geq \psi_d, \end{cases} \quad (2.6)$$

where $\psi_d \equiv \psi_{ge}$ is the air entry suction head at which air enters the capillary-porous body (i.e., the minimal capillary pressure the nonwetting phase must overpass to enter the pores occupied by the wetting phase) [L], $\lambda (> 0)$ is a pore-size distribution index [–].

Equally popular in terms of citation in the scientific literature is the *van Genuchten formula* (Van Genuchten 1980)

$$\bar{\theta}(\psi) = \begin{cases} \frac{1}{[1 + |\alpha\psi|^n]^m} & \psi < 0, \\ 1 & \psi \geq 0, \end{cases} \quad (2.7)$$

which in some cases yields more accurate (as compared with Eq. 2.6) description of experimental data. Here α , n and m are empirical parameters; α [L^{-1}] approximately equals the inverse of the air entry value for small m/n , while for large m/n this parameter roughly equals the inverse of the pressure head at the inflection point (Van Genuchten and Nielsen 1985); n (>1) is a parameter related to pore size distribution index [-]. To obtain a relatively simple predictive close-form analytical expression for the unsaturated hydraulic conductivity, Van Genuchten (1980) assumed a unique relationship between the parameters m and n , $m = 1 - 1/n$. This relationship between m and n implies a capillary pressure saturation curve with saturation in the low capillary pressure range to a greater extent than measurements (Corey 1994).

The relationship (2.7) is attractive in that, owing to its flexibility, it can describe a wider range of experimental curves $\psi = f(\theta)$, obtained for different types of sedimentary deposits. As compared with Eqs. 2.5 and 2.6, Eq. 2.7, better approximates the character of the curve $\psi = f(\theta)$ during the initial period of sample draining, when the suction head abruptly changes against a relatively small drop in saturation. Unlike (2.6), function (2.7) is continuous. However, an advantage of (2.6) is the fact that the parameter ψ_d in it has a clear physical meaning.

The relationship between ψ and θ is ambiguous: when a completely saturated sediment is being drained, the function $\psi(\theta)$ is such that each value ψ is associated with the maximum moisture content; while during saturation of a dry rock sediment, the same moisture content values will be associated with suction head with lesser absolute values. This reflects the effect of hysteresis of retention functions (Fig. 2.1). In general the hysteresis is caused by a change of the energy status of water when

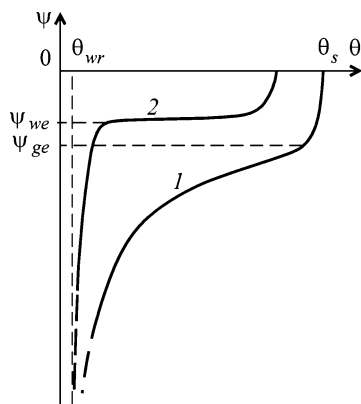


Fig. 2.1 Typical retention curves $\psi(\theta)$. 1 – drainage curve, 2 – wetting curve. ψ_{we} is the water entry suction head, ψ_{ge} is the air entry suction head, θ_{wr} is the residual water content

a wetting process is switched to a drying process or vice versa. The change in the energy status can be measured by a change in potential ψ . The hysteresis phenomena are of particular importance in the description of unsteady waves of moisture content during time-varying infiltration, as well as during the analysis of the instability of the wetting front (Nielsen et al. 1986). In this chapter, such phenomena are considered in their most general form.

The ability of soils and rocks to yield or to gain moisture with changing pressure head is characterized by the parameter

$$C(\psi) = d\theta/d\psi > 0, \quad (2.8)$$

called *specific moisture capacity* [L^{-1}]. It can be evaluated by differentiating the retention function $\theta(\psi)$. The specific moisture capacity can be defined precisely as the volume of water released from or taken into storage, per unit volume of vadoze zone, per unit change in pressure head (Stephens 1996).

2.1.1.3 Darcy's Law and Hydraulic Conductivity of Unsaturated Sediments and Rocks

Under conditions of vertical water movement through unsaturated single porosity subsurface materials, Darcy's law, also appropriately referred to as the Darcy–Buckingham equation (Narasimhan 2005; Raats and Genuchten 2006), is expressed as

$$q = -k(h) \frac{\partial h}{\partial z} = -k(\psi) \left(\frac{\partial \psi}{\partial z} + 1 \right), \quad (2.9)$$

where q is the *specific flux*, $k(\psi)$ is some coefficient of proportionality between the specific flux (Darcy velocity) and the gradient of hydraulic head which is called *unsaturated soil hydraulic conductivity*.

Considering the existence of a nonlinear relationship between ψ and θ , we can suppose that the hydraulic conductivity of an unsaturated soil or rock, k , is not constant and strongly depends on the volumetric water content. It varies from the value $k(\theta_0) = k_s$, which corresponds to the hydraulic conductivity at complete porous material saturation ($\theta = \theta_s$), to zero when the pores are dry (more exactly, the porous material at residual saturation $\theta = \theta_r$). The nonlinearity of the function

$$k = k(\theta) \text{ or } k = k(\psi)$$

is supported by a vast body of experimental data. A number of equations for the function k have been suggested by different researchers. Many of the theoretical and experimental findings can be rearranged to an exponential form of the *Averjanov (1950) equation*:

$$k(\bar{\theta}) = k_s \bar{\theta}^n, \quad (2.10)$$

where the exponent n has quite a wide range of values. Some of the pore macroscopic models predict $n = 2-4$ (Brutsaert 1967, 1968; Corey 1994; Leong and Rahardjo 1997). The coefficient n was found to be dependent on pore-size distribution and pore disconnectedness.

According to the tests of Brooks and Corey (1964) one may assume the following equation for unsaturated conductivity

$$k(\psi) = \begin{cases} k_s \left(\frac{\psi_d}{\psi} \right)^m & \psi < \psi_d, \\ k_s & \psi \geq \psi_d. \end{cases} \quad (2.11)$$

Since there exists a relationship between $\bar{\theta}$ and ψ_d/ψ in the form of Eq. 2.6, the unsaturated hydraulic conductivity can be represented as the power function (2.10). Experiment and theory demonstrate that n may be estimated from λ as $n = (2 + 3\lambda)/\lambda$. In equality (2.11) coefficient m can also be represented as a function of λ .

Substituting (2.5) into (2.10) we obtain the expression for the unsaturated hydraulic conductivity

$$k(\psi) = k_s e^{n\alpha\psi} \quad (\psi \leq 0), \quad (2.12)$$

suggested by Gardner (1958). Taking the logarithms of the left and the right parts of (2.12), we rewrite it as

$$\ln k(\psi) = \ln k_s + n\alpha\psi. \quad (2.12a)$$

Plots of (2.12a) in Fig. 2.2 reflect an interesting feature of the functional relationship $k(\psi)$ for two types of soils of mostly sand and clay composition (Gelhar 1993; Pease and Stormont 1996). When the moisture content is high (and, accordingly, $|\psi|$ is small), the ability of sand subsurface material to transfer water is also greater than that for clay-enriched sediments. Conversely, when the moisture content is low ($|\psi|$ is large), clay-enriched sediments, when not saturated, may be more permeable for water.

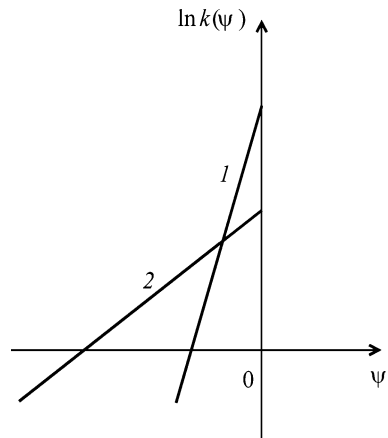


Fig. 2.2 Functional relationship $\ln k(\psi)$. 1 and 2 are sand and clay-enriched sediments, respectively

This effect, resulting from the difference between the absolute values of parameters (sands have high k_s and α , while compacted clayey materials have low k_s and α), should be taken into account in the studies of moisture migration in complexes of aerated stratified sediments as well as sediments (rocks) with dual-porosity structure, the fractures serve as high-permeability elements. Thus, it is clear that during dry periods (with low precipitation), moisture in the aeration zone presented by fractured-porous rocks would mostly migrate through low-permeability pore blocks, because the estimated moisture transfer coefficient for them will be larger than for considerably drained (dewatered) fractures. In rainy periods, when fissures are filled with water, they should contribute most to moisture transfer (Chap. 7).

In general there are two major approaches to obtain the hydraulic conductivity function for an unsaturated subsurface material: (a) empirical fitting of equations to measured lab or field data, (b) statistical models which can be used to predict the hydraulic conductivity function when the saturated hydraulic conductivity k_s and the soil-water characteristic curves are available. In particular, a statistical model analysis results in the following relationship for hydraulic conductivity for the van Genuchten retention curve (Van Genuchten 1980):

$$k(\bar{\theta}) = k_s \sqrt{\bar{\theta}} \left(1 - (1 - \bar{\theta}^{1/m})^m \right)^2, \quad (2.13)$$

where k_s is the hydraulic conductivity at saturation [LT^{-1}]; the unsaturated hydraulic properties are approximated reasonably well with the more restricted case where $m = 1 - 1/n$ (Van Genuchten and Nielsen 1985). Equation 2.13 was obtained by substituting Eq. 2.7 into an expression derived by Mualem (1976).

Taking into account hysteresis in the water retention functions (Sect. 2.1.1.2), one may expect the relationship between unsaturated hydraulic conductivity and pressure head also to be hysteretic. Obviously, problems in which hysteresis may be important to consider involve periods of both wetting and drying, such as can occur during infiltration and subsequent redistribution of a square-wave pulse of infiltrated water (Stephens 1996). Such finite pulse of water cannot accurately be modeled by assuming as input parameters either the wetting or drying unsaturated hydraulic conductivity curves.

2.1.1.4 Soil Water Diffusivity

Expression (2.9) for moisture flux can be represented in the alternative form:

$$-q = k(\theta) \frac{d\psi}{d\theta} \frac{\partial \theta}{\partial z} + k(\theta) = D(\theta) \frac{\partial \theta}{\partial z} + k(\theta), \quad (2.14)$$

where

$$D(\theta) = \frac{k(\theta)}{d\theta/d\psi}, \quad d\theta/d\psi > 0. \quad (2.14a)$$

The representation (2.14) has an advection–dispersion form: the first term in the right part of the latter identity (2.14) reflects the diffusivity of moisture flux at the expense of capillary-adsorption forces; therefore, the parameter $D(\theta)$ (2.14a) is referred to as *soil water (moisture) diffusivity* [L^2T^{-1}]; water diffusivity does not exist near saturation (i.e., as $D(\theta)$ approaches ∞) since $C(\psi)$ approaches zero; the second term in the right part of (2.14) is the gravity-induced (advection) transfer of moisture under unit gradient.

Similar to $k(\theta)$, function $D(\theta)$ can be formulated in terms of macroscopic pore models (Corey 1994; Singh 1997). Combining Eqs. 2.5, 2.10 with Eq. 2.14a and Eqs. 2.6, 2.11 with Eq. 2.14a gives

$$D(\bar{\theta}) = \frac{k_s}{\alpha \Delta \theta} \bar{\theta}^{n-1} \text{ and } D(\bar{\theta}) = \frac{k_s |\Psi_d|}{\lambda \Delta \theta} \bar{\theta}^{\frac{m-\lambda-1}{\lambda}} \quad (2.15)$$

for Averjanov and Gardner, Brooks–Corey models, respectively. Thus, the soil water diffusivity may be described as a power function of relative water content; the difference $\Delta \theta = (\theta_s - \theta_r)$ is the *moisture capacity*, a parameter which appears in many analytical formulas related to water and solute transport in unsaturated zone.

The nonlinear soil water diffusivity as a power function of relative water content

$$D(\theta) = D_s \bar{\theta}^\gamma \quad (2.16)$$

has been used over the last few decades by a number of soil physicists; here $D_s = D(\theta_s)$ (saturated soil water diffusivity) and γ are constants. Some researchers employed the exponential diffusivity law for function $D(\theta)$, postulating (Parlange 1980; Singh 1997)

$$D(\theta) = ae^{b\bar{\theta}}, \quad (2.17)$$

where a and b are empirical coefficients.

Formulas (2.16) and (2.17) illustrate the basic difficulty of water movement in soil, i.e. D increases very rapidly with θ , corresponding to a profile where most of change in θ occurs in a narrow zone $\theta^0 \leq \theta \leq \theta_s$. That is totally different from a molecular diffusion process (Sect. 1.1.2) with near-constant diffusivity. Hence standard linearization techniques are inapplicable to calculate the profile $\theta(z)$ based on a given single value of D (Parlange 1980).

2.1.2 Continuity Equation and its Major Representations

The equation of continuity (or mass conservation) is

$$\frac{\partial \theta \rho_w}{\partial t} = \nabla \cdot (\rho_w \mathbf{q}). \quad (2.18)$$

Assuming that the density of water ρ_w remains constant, the equation of continuity (2.18) for 1D water flow in z direction becomes:

$$\frac{\partial \theta}{\partial t} + \frac{\partial q}{\partial z} = 0. \quad (2.19)$$

Expressing the infiltration rate in terms of the hydraulic head function (2.2), we come to the equation

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left(k(h) \frac{\partial h}{\partial z} \right), \quad (2.20)$$

which is of a fundamental character and is often referred to as *Richards equation*. Clearly, it is based on the continuity equation and Darcy's law (Richards 1931). The Richards equation for soil moisture movement holds a very important place in modern theoretical and applied hydrology, in particular providing a basis for studies of global water cycle and the assessment of groundwater protection against the industrial contamination. The Richards equation (2.20) allows further transformations (representations), whose specific features are determined by the character of problems to be solved and the form of the available parametric (experimental) functions $\psi - \theta - k$.

Thus, setting $\partial \theta / \partial t = (d\theta/d\psi) \partial \psi / \partial t$, we obtain the ψ -based formulation of Richards equation (pressure head-based Richards equation):

$$\text{or} \quad C(\psi) \frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z} \left(k(\psi) \frac{\partial \psi}{\partial z} \right) + \frac{dk(\psi)}{d\psi} \frac{\partial \psi}{\partial z}, \quad (2.21)$$

where $C(\psi) = d\theta/d\psi > 0$ is defined as the specific moisture capacity function (2.8). The coefficients of Eq. 2.21 involve two highly non-linear functions related to the soil water potential.

Once the flux q in the continuity Eq. 2.19 is determined, from Eq. 2.14 we obtain the so-called θ -based formulation of Richards equation (2.20) (Gardner 1958; Vanderborght et al. 2005):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left(D(\theta) \frac{\partial \theta}{\partial z} \right) + \frac{dk(\theta)}{d\theta} \frac{\partial \theta}{\partial z}. \quad (2.22)$$

The dependence of D and k on θ renders Eq. 2.22 highly nonlinear.

The moisture-based Eq. 2.22 is appropriate for describing flow in unsaturated homogeneous media only such that $\psi(\theta)$ is single-valued. This equation can not be used to describe water flow under saturated condition (Corey 1994). Therefore the pressure-based form (2.21) more suitable for variably-saturated soil (including fully saturated conditions) and spatially heterogeneous soils.

Finally, the "mixed" Richards equation has the form:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left(k(\psi) \frac{\partial \psi}{\partial z} \right) + \frac{\partial k(\psi)}{\partial z}. \quad (2.23)$$

Koo and Suh (2001) note that the use of the mixed Eq. 2.23 for the numerical solution of moisture transfer problems (especially, two- and three-dimensional ones) allows one to avoid the shortcomings of the implementation of algorithms based on the two previous representations of the equation in question.

To make the presentation of material general, we give here a three-dimensional form of the basic equation of mass transport in the aeration zone:

$$\frac{\partial \theta}{\partial t} = \nabla \cdot [\mathbf{k}(\psi) \cdot \nabla(\psi + z)], \quad (2.24)$$

where $\mathbf{k}(\psi)$ is a second-order tensor of the moisture transfer; the z -axis is directed vertically upward.

In conclusion we make a comment. The functional relationships $\psi - \theta$ and $k - \psi(\theta)$ used in the mathematical formulation of moisture transfer problems are evaluated from experiments carried out under the conditions close to thermodynamic equilibrium because of the long duration of experiments: to obtain experimental curves similar to those graphically represented in Fig. 2.1 commonly requires several days or weeks. Therefore, the parameters that characterize the kinetic stage of the process, preceding the attainment of $\psi - \theta$ capillary equilibria, commonly are not involved in the interpretation procedures. However, the processes in nature that accompany soil drainage or saturation often take a few hours or days. Therefore, the classic description of such processes on the basis of the Richards equation, which makes no allowance for the real dynamics (kinetics) of the establishment of capillary equilibrium $\psi - \theta$, can be not quite adequate. Such effects were called *dynamic* (Hassanizadeh et al. 2002).

The correct use of experimental equilibrium relationships may require in some cases the inclusion into the model of some kinetic parameters to allow one to more thoroughly study the unsteady moisture transfer in the cases when the rates of changes in the moisture content function (or saturation $S = \theta/\phi$) are large. Relationships between the static ($\psi_{\text{stat}} \equiv \psi = \psi(S)$) and dynamic (ψ_{din}) suction pressures have been proposed in the form of the kinetic equation (Hassanizadeh et al. 2002):

$$\psi_{\text{din}} = \psi(S) - \frac{\tau}{\phi \rho g} \left(\frac{\partial \theta}{\partial t} \right), \quad (2.25)$$

where τ is a relaxation factor of the system [$\text{ML}^{-1}\text{T}^{-1}$], which can vary depending on the saturation of the medium; its values vary within the orders of 10^4 – 10^7 kg/ms.

The equality (2.25) allows us to transform the initial equations of moisture transfer, thus taking into account the dynamic effects. The need for this can arise in the analysis of significantly unstable moisture flows in fine-grained media with high entry capillary pressure, as well as in the description of the instability of moisture transfer front. However, the traditional formulation of the problem of moisture transfer in porous medium under the effect of gravity (advection) and adsorption-capillary forces (sometimes, conventionally referred to as diffusion) is sufficient in the overwhelming majority of practically significant cases.

2.1.3 *Particular Solutions for Moisture Migration and Their Analysis*

2.1.3.1 Problem Formulation

The moisture transfer equations given above are essentially nonlinear, since their coefficients depend on the functions sought for (ψ or θ). This creates apparent difficulties for the search of their solutions in a closed analytical form. The original differential equations become more complicated because of the inclusion of additional source terms to account for moisture losses from the transition zones (pores, macropores, and fissures) due to evapotranspiration (evaporation and consumption by plant roots) and the saturation of porous rock blocks in contact with those zones (Chap. 7).

The search for solutions of the Richards equation, which are adapted to real situations, by numerical methods is a complex problem (Van Dam et al. 2004). This is due not only to the strong nonlinearity of the process being simulated, but also to very wide variation ranges of the control variables (functions). For example, with moderate moisture content of near-surface sedimentary deposits in the aeration zone, the suction pressure ψ can reach -10^6 cm. Heavy precipitation or accidental spills of a liquid can increase porous material moistening within a few minutes, resulting in a pressure drop to zero. At the same time, the values of the moisture transfer coefficient increase by 5–8 orders of magnitude. The modeling of such events requires the time steps to be very small and very strict convergence criteria for the solution of the Richards equation to be met (Van Dam et al. 2004).

In view of the further practical application, the mathematical formulation of the problem should reflect the specific hydrogeological and geomorphological conditions of individual areas, the direction of the process (whether the aeration zone is being drained or saturated – because of the hysteresis of parameter functions), and the regime and rate of infiltration recharge. One should also take into account that, although Eqs. 2.21 and 2.22 have been derived from similar physical assumptions, their application conditions do not coincide, i.e., they are not completely equivalent (Ravi and Williams 1998). However, notwithstanding the restrictions for the use of Eq. 2.22, it is convenient for the analysis of moisture migration in homogeneous media.

In the ideal case, the initial condition ($t = 0$) should specify the initial distribution of moisture or the suction pressure:

$$\theta(z, t = 0) = \theta^0(z), \quad \psi(z, t = 0) = \psi^0(z). \quad (2.26)$$

In the case of infiltration problems, the boundary conditions (the z -axis is directed vertically downward, $z = 0$ on the surface) can be of the first, second, or third type, respectively:

$$\theta(z = 0, t) = \theta_0(t), \quad \psi(z = 0, t) = \psi_0(t), \quad (2.27a)$$

$$q(z = 0, t) = q_0(t), \quad (2.27b)$$

$$k(\theta) - D(\theta) \frac{\partial \theta}{\partial z} = q_0(t), \quad k(\psi) \left(1 - \frac{\partial \psi}{\partial z} \right) = q_0(t). \quad (2.27c)$$

The correct specification of boundary conditions on the upper boundary is often problematic when groundwater level varies considerably and the land surface can be ponded in some moments. For example, after water level in the aquifer drops below this surface and the near-surface soil layer becomes dry, the suction pressure abruptly rises, creating difficulties with the convergence of numerical solutions of the Richards equation describing this process. Generally, effective procedures for “switching” boundary conditions from the first to the second type and back should be among the necessary options of mathematical models intended for studying such situations.

In the strict formulation, the boundary condition on the lower boundary of the aeration zone should specify the conjunction with the water-saturated rock formations, i.e., the aquifer (drainage condition). However, the process can be sometimes considered as taking place in a semi-infinite medium. In such cases, it is better to assume the z -axis to be directed vertically downward. Accordingly, the gravitational (advective) terms in the initial Eqs. 2.21, 2.22, and 2.23 change their signs to the opposite. A complete analysis of water redistribution in soil should take into account capillary hysteresis effects.

The problem of search for analytical solutions of the Richards equation is the subject of a vast body of scientific literature (Philip 1957a, b; Youngs 1957; Broadbridge and White 1988; Broadbridge 1990; Barry and Sander 1991; Ross and Parlange 1994; Salvucci 1996; Parlange et al. 1997, 1999; Wang et al. 2003; Wiltshire and El-Kafri 2004). The final analytical solutions are complicated, especially when the initial conditions are heterogeneous and the input (boundary) functions have a “burst” character (i.e., when the hysteresis of the parametric function $\psi - \theta$ manifests itself in full measure). Therefore, infiltration processes are most often described by numerical models, which allow the hysteresis of soil-water retention functions to be taken into account. However, some useful results can be obtained with simplified physical models, neglecting certain mechanisms of moisture transfer at some process stages.

Although studying water motion in the unsaturated zone requires the use of unsteady state problems, the steady state formulation of the problem may be of interest as well. We will start our analysis from this case.

2.1.3.2 Steady-State Water Flow Models

Formula (2.9) yields two consequences reflecting some specific features of the behavior of function ψ in different conditions.

1. In the absence of moisture transfer in the aeration zone, when we can assume $q = 0$, the gradient $\partial \psi / \partial z = -1$ ($\partial h / \partial z = 0$), or $\psi = z_0 - z$, i.e., the suction

height is numerically equal to the elevation above the reference plane ($z = z_0$), for example, above the groundwater level; if $z_0 = 0$, then $\psi = -z$. This fact implies that the moisture distribution in the capillary zone should correspond to the soil water retention function $\theta(z) = \theta(\psi)$.

2. In the case of *steady-state moisture transfer* (water-application rate $q = \text{const}$) the distribution of the suction pressure depends on the form of function $k(\psi)$ and is determined by the integral equality:

$$z - z_0 = - \int_0^{\psi} \frac{d\psi}{1 + q/k(\psi)}, \quad (2.28)$$

where the integral in (2.28) can have an analytical representation in algebraic functions when $k(\psi)$ are available (Gardner 1958).

In the general steady-state formulation, the profile of the suction pressure $\psi(z)$ can be calculated by applying the method of successive direct fitting (Ho 2001): with known pressure $\psi(z_i)$ in point z_i , we search for the pressure $\psi(z_{i+1})$ in the upstream point z_{i+1} by integrating function (2.28) over the interval $[\psi(z_i), \psi(z_{i+1})]$ ($\psi(z_{i+1})$ is the sought-for upper integration limit), i.e.:

$$z_{i+1} = z_i - \int_{\psi(z_i)}^{\psi(z_{i+1})} \frac{d\psi}{1 + q/k(\psi)}. \quad (2.29)$$

Moreover, the solution (2.29) can be extended to the case of steady-state moisture transfer in a stratified system by choosing the values of $\psi(z)$ from $\psi(z_1)$ to $\psi(z_n)$ by calculation through all lithological beds with the value of function $k(\psi)$ corresponding to the layer with a number, say, Ω , $\Omega = 1, 2, \dots, m$ (m is the number of layers) used to calculate the integral function (Ho 2001):

$$z_{i+1}^{\Omega} = z_i^{\Omega} - \int_{\psi^{\Omega}(z_i)}^{\psi^{\Omega}(z_{i+1})} \frac{d\psi}{1 + q/k^{\Omega}(\psi)}. \quad (2.30)$$

When the calculation process reaches an interface between two layers, the pressure at the bottom of each layer (with bottom-upward numeration) is taken equal to the pressure at the top of the underlying layer, i.e., the boundary condition for each lithological contact has the form:

$$z_i^{\Omega+1} = z_i^{\Omega}; \psi(z_i^{\Omega+1}) = \psi(z_i^{\Omega}). \quad (2.31)$$

The calculated profile $\psi(z)$ allows one, taking into account the functional form of the relationship $\psi(\theta)$, to determine the distribution of moisture over the depth; hence, given the Darcy velocity (q), one can find variations in the real migration velocity $u(z) = q/\theta(z)$.

2.1.3.3 A Water Absorption Model (Moisture Movement Without Gravity)

If the gravity component is neglected, as is reasonable in the case of infiltration into relatively dry soils at the initial stages of moisture front formation, the Eq. 2.22 can be reduced to

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left(D(\theta) \frac{\partial \theta}{\partial z} \right), \quad (2.32)$$

known as *moisture diffusivity equation* (Bear and Cheng 2010).

As is proved in the theory of differential equations (Polyanin et al. 2005), the Eq. 2.32 has a self-similar solution in the form

$$\theta(z, t) = \theta(\lambda), \text{ where } \lambda = \frac{z}{\sqrt{t}} \quad (2.33)$$

is the so-called *Boltzmann transformation*, combining the variables z and t (Philip 1957a; Lagan 2001). The profiles of self-similar solutions in different time moments can be obtained from one another by a similarity transformation. Each value λ is associated with a single value θ , and the conditions $\lambda = \text{const}$ and $z \sim \sqrt{t}$ hold for constant moisture content.

The substitution of the new variable $\lambda = z/\sqrt{t}$ into the Eq. 2.32 allows this equation to be transformed into the ordinary differential equation

$$\frac{\lambda}{2} \frac{d\theta}{d\lambda} + \frac{d}{d\lambda} \left(D(\theta) \frac{d\theta}{d\lambda} \right) = 0, \quad (2.34)$$

with the following boundary conditions:

$$\theta(\lambda = 0) = \theta_0, \theta(\lambda \rightarrow \infty) = \theta^0. \quad (2.35)$$

The transition from (2.32) to (2.34) implied:

$$\frac{\partial}{\partial z} = \frac{\partial \lambda}{\partial z} \frac{\partial}{\partial \lambda} = \frac{1}{\sqrt{t}} \frac{d}{d\lambda}, \frac{\partial}{\partial t} = \frac{\partial \lambda}{\partial t} \frac{\partial}{\partial \lambda} = -\frac{1}{2} \frac{\lambda}{t} \frac{d}{d\lambda}. \quad (2.36)$$

The integration of (2.34) yields the integro-differential equation (Bruce and Klute 1956; Philip 1957a)

$$\int_{\theta^0}^{\theta} \lambda d\theta = -2D(\theta) \frac{d\theta}{d\lambda}, \quad (2.37)$$

which can be easily solved by iteration numerical methods.

Equation (2.37) shows that Boltzmann variable $\lambda(\theta)$ linearizes Eq. 2.32 to give the solution for diffusivity at water content θ' , in other words, $D(\theta')$ can be quantified if $\lambda(\theta)$ is measured

$$D(\theta') = -\frac{1}{2} \left(\frac{d\lambda}{d\theta} \right)_{\theta=\theta'} \int_{\theta^0}^{\theta'} \lambda(\theta) d\theta; \quad (2.38)$$

the Eq. 2.38 is known as the [Bruce and Klute \(1956\)](#) equation ([Stephens 1996](#); [Selker et al. 1999](#)).

The function

$$S \equiv S(\theta_0, \theta^0) = \int_{\theta^0}^{\theta_0} \lambda(\theta) d\theta, \quad (2.39)$$

which is determined by the left part of Eq. 2.37 for $\theta = \theta_0$ and called by [Philip \(1957b\)](#) the *soil water sorptivity* [$LT^{-1/2}$], is often an important component of the theoretical analysis of vertical infiltration in the absence of the effect of gravity. If moisture content θ at $z = 0$ is maintained at zero suction by free water being made available in excess at $z = 0$, then $\theta = \theta_s$, that is the most commonly discussed condition ([Philip 1957a](#); [Williams et al. 1998](#)).

The sorptivity S quantifies the effect of capillarity on liquid movement in a soil. The water sorptivity of a soil is a property identified by [Philip \(1957b\)](#) as the critical quantity governing the infiltration at *early time*. For liquid infiltration into soil, S is a parameter that integrates several factors describing the capacity of the soil to imbibe water at early time, such as initial dryness of the soil and water content behind the infiltrating front.

Two major characteristics of the infiltration process, describing its *dynamics* (see Sect. 2.1.3.6) are related with this characteristic: *the cumulative infiltration* (the accumulated volume of the imbibed liquid per unit surface area), $I(t)$ [L], and *the infiltration rate* (or *infiltration capacity*) at time t (the volume of liquid that seeps from the unit area of the surface per unit time) $i(t)$ [LT^{-1}]. The sorptivity is a parameter that accounts for the effect of capillary forces on the unsteady infiltration process, which governs the variations of soil moisture content from the background (initial) value θ^0 to the boundary value θ_0 , i.e., the parameter S characterizes the state of the aeration zone (or soil) under specific landscape–climatic conditions.

At the initial stages of infiltration:

$$I(t) = \int_{\theta^0}^{\theta_0} z(\theta, t) d\theta = S\sqrt{t}, \quad i(t) = \frac{dI(t)}{dt} = \frac{1}{2} \frac{S}{\sqrt{t}}. \quad (2.40)$$

Attempts were made in some works to derive analytical expressions for parameter S , which would agree with calculated and experimental data ([Brutsaert 1976](#)). In order to find a relationship between the sorptivity and diffusivity, [Wang et al. \(2006\)](#) used the assumption of [Parlange \(1971a\)](#) to change Eq. 2.32 to the following

$$\frac{\partial z}{\partial t} + \frac{\partial}{\partial \theta} \left[\frac{D(\theta)}{\partial z / \partial \theta} \right] = 0. \quad (2.41)$$

Assuming $\theta_0 = \theta_s$ and integrating (2.41) for the gradient function

$$i = -D(\theta) \frac{\partial \theta}{\partial z} \approx -D(\theta_s) \left(\frac{\partial \theta}{\partial z} \right)_{z=0}, \quad (2.42)$$

one can get (Wang et al. 2006)

$$i = \frac{1}{\sqrt{2t}} \left[\int_{\theta^0}^{\theta_s} \theta D(\theta) d\theta \right]^{1/2}. \quad (2.43)$$

Comparing Eq. 2.43 with Eq. 2.40 yields

$$S \equiv S(\theta_s, \theta^0) = \left[2 \int_{\theta^0}^{\theta_s} \theta D(\theta) d\theta \right]^{1/2}. \quad (2.44)$$

Equation (2.44) defines the relationship between S and D and coincides with a result obtained by Parlange (1971a). For the generalized exponential model (2.16), Eq. 2.44 is transformed as

$$S = \frac{\sqrt{2}}{\sqrt{\gamma+2}} [D_s ((\theta_s)^{\gamma+2} - (\theta^0)^{\gamma+2})]^{1/2}. \quad (2.45)$$

An approximate solution of (2.32) can be obtained in the form of a *traveling wave solution*:

$$\theta(z, t) = \theta(\eta), \quad \eta = z - u^w t, \quad (2.46)$$

where u^w is a constant propagation velocity of the moisture wave. The solution (2.46) has a self-similar front of moisture content, and solution profiles in different moments can be obtained from one another by a shift transformation (Polyanin et al. 2005). The shape front observed at any time repeats the shape front observed at a previous moment but with a shift along the z -axis, depending on the wave velocity u^w .

Substituting Eq. 2.46 into the initial Eq. 2.32 yields, as well as the Boltzmann transformation, the ordinary differential equation

$$\frac{d}{d\eta} \left(D(\theta) \frac{d\theta}{d\eta} \right) + u^w \frac{d\theta}{d\eta} = 0. \quad (2.47)$$

Its integration with constant boundary conditions yields

$$-\int_{\theta^0}^{\theta} \frac{D(\theta) d\theta}{u^w (\theta_0 - \theta)} = \eta, \quad (2.48)$$

where $\theta^0 = \theta(z = \infty)$, $\theta_0 = \theta(z = -\infty)$.

Consider a possible transformation of this solution in the case of low initial moisture content, when $\theta^0 = \theta_r$. Let the dependence of functions ψ and k on the relative moisture content ($\bar{\theta}$) be determined by (2.5) and (2.10), while $u^w = k(\theta_0)/(\theta_0 - \theta_r)$. Then, considering the functional form of the soil water diffusivity $D(\theta)$ (2.15), we obtain:

$$\int_0^{\bar{\theta}} \frac{\bar{\theta}^k}{1 - \bar{\theta}} d\bar{\theta} = -\bar{\eta}, \quad k = n - 1, \quad \bar{\eta} = \frac{\alpha\eta}{\beta}, \quad \bar{\theta} = \frac{\theta - \theta_r}{\theta_0 - \theta_r}, \quad (2.49)$$

$$\beta = \frac{\theta_s - \theta_r}{\theta_0 - \theta_r}, \quad u^w = \frac{k(\theta_0)}{\theta_0 - \theta_r} = \frac{k_s}{\beta^{n-1}\Delta\theta}, \quad \Delta\theta = \theta_s - \theta_r. \quad (2.49a)$$

The integration of (2.49) yields the solution of the problem as the following implicit function of $\bar{\theta}$:

$$\sum_{m=0}^{k-1} \frac{\bar{\theta}^{k-m}}{k-m} + \ln(1 - \bar{\theta}) = \bar{\eta}, \quad (2.50)$$

for example, at $n = 3$ ($k = 2$)

$$\frac{\bar{\theta}^2}{2} + \bar{\theta} + \ln(1 - \bar{\theta}) = \bar{\eta}. \quad (2.51)$$

Similar solution was obtained for the soil water diffusivity (2.15) from the Brooks–Corey model.

The use of the solution (2.37), as well as of many other solutions obtained for the moisture transport equation in the closed analytical form, is restricted by the assumption that the initial condition is homogeneous ($\theta^0 = \text{const}$). In the case where $\theta^0 = \theta(z) \neq \text{const}$, the following approach can be recommended for obtaining approximate solutions (Witelski 1998). The presence of the initial water distribution in the soil is taken into account in the analytical solution by introducing a time-shift, τ , which advances the wetting front:

$$\theta(z, t) = \begin{cases} \theta(z/\sqrt{t + \tau(t)}) & z < z_*(t), \\ \theta^0(z) & z \geq z_*(t), \end{cases} \quad (2.52)$$

where $\theta[\xi(t + \tau)]$ is the solution obtained under the condition $\theta^0 = 0$ with the use of Boltzmann transformation (ξ), in which the duration of the process is increased by $\tau(t)$; $z_*(t)$ is the position of the interface or wetting front. The time shift, $\tau(t)$, is calculated from the initial moisture distribution and the average soil water diffusivity:

$$\tau(t) = \int_0^{z_*} z \theta^0(z) dz / \int_0^{\xi_*} \xi \theta(\xi) d\xi. \quad (2.53)$$

For degenerate diffusion problems, one can calculate a dynamic time-shift function yielding a good approximate solution for all times (Witelski 1998).

2.1.3.4 Gravity-Induced Moisture Advection

Consider another utmost case where water moves under gravity, and capillary forces can be neglected ($\partial\psi/\partial z \ll 1$), i.e.

$$q = -k(\psi) \left(\frac{\partial\psi}{\partial z} - 1 \right) = k(\psi) > 0, \quad (2.54)$$

that is, the Darcy law (2.9), written for the case where the z -axis is directed vertically downward.

Let water input rate be less than the saturated hydraulic conductivity, $q(z=0) = q_0 < k_s$. It appears physically obvious that in this case the applied infiltration rate q_0 is not sufficient to maintain water outflow from the recharge boundary under the effect of gravity with soils or rocks remaining fully water-saturated, i.e., the infiltration takes place under partial saturation of the pore space $\theta = \theta_w < \theta_s$, while the rest of it remains filled with air.

From the balance considerations, the propagation velocity of the *wetting front* (the interface between zones with volumetric moisture content θ_w and θ^0 , Fig. 2.3) is determined by the kinematic equation

$$u^w = \frac{dz}{dt} = \frac{q_0}{\theta_w - \theta^0}. \quad (2.55)$$

Formula (2.55) is derived from the assumption that the moisture distribution is piston-like.

Given the analytical dependence of the unsaturated hydraulic conductivity on moisture content $k = f(\theta)$, the inverse function $\theta = f^{-1}(k)$ can be found, allowing one to evaluate the moisture content θ_w on the wetting front and behind

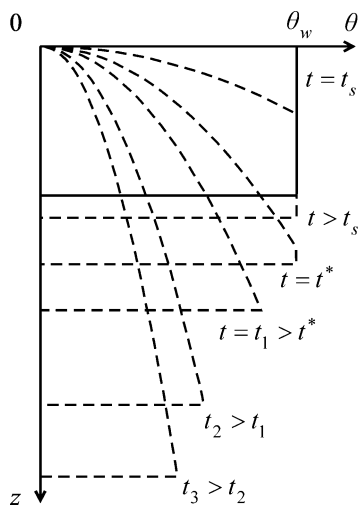


Fig. 2.3 Moisture distribution in different moments for a square pulse of flux density input, $\theta(z=0, t)$. Solid lines correspond to a moisture profile at the end of infiltration $t = t_s$, dashed lines correspond to a desaturation profile for $t > t_s$

it ($z \leq u^w t$) $\theta_w = f^{-1}(q_0)$, which enters the expression (2.55). Thus, for the Averjanov formula (2.10), which is widely used in hydrogeological calculations, we have:

$$\bar{\theta}_w = \left(\frac{q_0}{k_s} \right)^{\frac{1}{n}}. \quad (2.56)$$

Now the expression for the real velocity of vertical moisture transfer at $\theta_r \ll \theta^0$ becomes

$$u^w = \frac{q_0}{\theta_s (q_0/k_s)^{1/n} - \theta^0}. \quad (2.57a)$$

If we assign $\theta^0 = \theta_r$, then

$$u^w = \frac{k_s}{\Delta\theta} \left(\frac{q_0}{k_s} \right)^{\frac{n-1}{n}} = \frac{k_s}{\Delta\theta} \bar{\theta}_w^{n-1}, \quad (2.57b)$$

$\Delta\theta = \theta_s - \theta_r$ (moisture capacity). Since $n > 1$, the flow velocity u^w increases with increasing soil saturation. This implies that the wetting front is of *self-sharpening* character.

The cessation of infiltration from the surface ($q_0 = 0$) in moment $t = t_s$ results in the formation of a *drying front* (Fig. 2.3). In Fig. 2.3a piston-like distribution is shown at the end of infiltration ($t = t_s$). The expanding drying front ($t > t_s$) forms where air replaces liquid at the interface between the dry upper soil and the top of the descending fluid phase. Because of the nonlinearity of the process, the drying front tends to disperse. An equation describing the spreading of the drying front results from the continuity Eq. 2.19 in which the specific flux is determined by (2.54):

$$\frac{\partial\theta}{\partial t} + \frac{dk(\theta)}{d\theta} \frac{\partial\theta}{\partial z} = 0. \quad (2.58)$$

Determining $k(\theta)$ from (2.10), we obtain

$$\Delta\theta \frac{\partial\bar{\theta}}{\partial t} + nk_s \bar{\theta}^{n-1} \frac{\partial\bar{\theta}}{\partial z} = 0, \quad (2.59)$$

or

$$\frac{dt}{\Delta\theta} = \frac{dz}{nk_s \bar{\theta}^{n-1}} = \frac{d\bar{\theta}}{0}. \quad (2.60)$$

The integration of (2.60) with $z(t - t_s = 0) = 0$ yields the characteristic solution

$$z(t) = u^d(\theta)(t - t_s) = \frac{nk_s \bar{\theta}^{n-1}}{\Delta\theta} (t - t_s) \text{ along the characteristic } \bar{\theta} = \text{const.} \quad (2.61)$$

For $t > t_s$, the moisture content profile is determined by two simultaneous processes (Fig. 2.3): drying at the top of the fluid pulse and continuous downward propagation of the wetting front at the bottom of the pulse (Lessoff and Indelman 2004). Since $n > 1$, as it follows from comparison of Eqs. 2.57b and 2.61, the drying front propagates faster than the wetting front and eventually overtakes the wetting front at the meeting time t^* , which can be determined from the simple equation $u^w_{t^*} = u^d(t^* - t)$, where u^w and u^d are determined from Eqs. 2.57b and 2.61 assuming in the latter $\bar{\theta} = \bar{\theta}_w$. In particular, from the above it follows: $t^* = nt_s/(n - 1)$.

After the wetting and dry fronts meet ($t > t^*$), the front location obeys both (2.57b) and (2.61), whereas the common front saturation $\bar{\theta}_f(t)$ satisfies the equation (Lessoff and Indelman 2004)

$$\frac{d\bar{\theta}_f}{dt} = \frac{1}{n} \frac{\bar{\theta}_f}{t - t_s}. \quad (2.62)$$

Since, according to (2.56), $\bar{\theta}_f(t^*) = (q_0/k_s)^{1/n}$, Eq. 2.62 has the solution

$$\bar{\theta}_f(t) = \left(\frac{q_0}{k_s}\right)^{\frac{1}{n}} \left(\frac{t^* - t_s}{t - t_s}\right)^{\frac{1}{n}}, \quad t^* = \frac{n}{n-1}t_s. \quad (2.63)$$

One may see that as time goes to infinity, the wetting front unboundedly moves downwards and the moisture content approaches the residual value θ_r everywhere (Lessoff and Indelman 2004).

If the value of hydraulic conductivity k_s is small relative to the applied infiltration rate, i.e., $q_0/k_s > 1$, a positive pore water pressure appears at the ground surface after certain time and the shallow soil becomes saturated (Ng and Menzies 2007). This is a result of the small k_s , which prevents some of the rainwater from infiltrating into the soil and results in the development of ponding on the ground surface (Ravi and Williams 1998; Ng and Menzies 2007).

2.1.3.5 Green–Ampt Model

When considering the piston-like (with an abrupt interface) motion of moisture in the aeration zone (Fig. 2.4a), we can try to take into account the joint effect of capillary-adsorption and gravitational components. Infiltration is hardly affected by gravity if the soil surface is ponded (even at the early stages of the process).

Suppose that the pressure in the liquid at the interface between the media ($z = 0$) is determined by the atmospheric pressure and the pressure of the liquid layer covering the surface (Fig. 2.4b). This condition corresponds to the following expression written in hydraulic head functions:

$$h(0) = h_g + h_0, \quad (2.64)$$

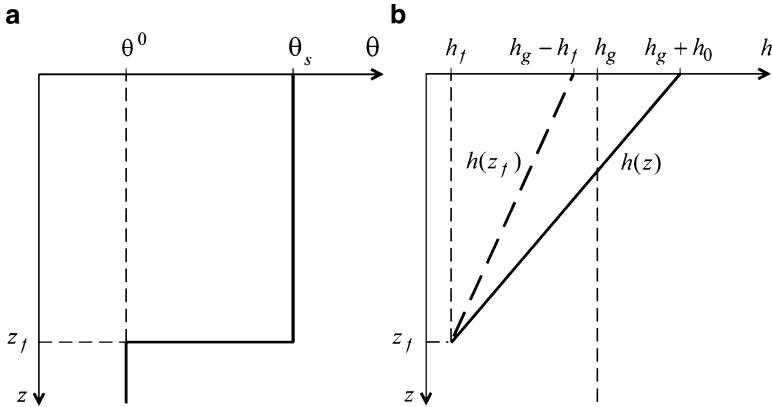


Fig. 2.4 The distribution of (a) volumetric moisture content and (b) the hydraulic head at piston-like motion of moisture in the aeration zone

where h_g is the head determined by the atmospheric pressure, h_0 is the depth of the water layer. Now, the head on the moving infiltration-water front, whose position is determined by the current coordinate $z_f(t)$, will be

$$h(z_f) = h_g - h_f - z_f, \quad (2.65)$$

where $h_f = -\psi_f$ is the capillary head at the moistening front – a characteristic, which, strictly speaking, should be related with the measurable physical parameters of the soil or rocks (Neuman 1976; Kao and Hunt 1996; Williams et al. 1998). An approximate expression for h_f can be also obtained from the phenomenological capillary model of porous medium (Kao and Hunt 1996).

Thus, the hydraulic gradient is:

$$\frac{dh}{dz} = -\frac{h(0) - h(z_f)}{z_f} = -\frac{h_0 + h_f + z_f}{z_f}. \quad (2.66)$$

The equation for the head function $h(z)$ ($0 \leq z < z_f$) (Fig. 2.4b):

$$h(z) = (h_g + h_0) + \frac{dh}{dz}z = (h_g + h_0) - \frac{h_0 + h_f + z_f}{z_f}z. \quad (2.67)$$

The migration velocity of the leading edge:

$$u^w = \frac{dz}{dt} = -\frac{k(\theta_s)}{\theta_s - \theta^0} \frac{dh}{dz} = \frac{k(\theta_s)}{\Delta\theta} \left(1 + \frac{h_0 + h_f}{z_f} \right), \quad \Delta\theta = \theta_s - \theta^0, \quad k(\theta_s) \equiv k_s. \quad (2.68)$$

Integrating the ordinary differential Eq. 2.68 yields the following formula

$$t = \frac{\Delta\theta}{k_s} \left[z_f - (h_0 + h_f) \ln \left(1 + \frac{z_f}{h_0 + h_f} \right) \right], \quad (2.69)$$

known as the *Green–Ampt solution*. This solution, which was published in 1911 (Green and Ampt 1911), is among the fundamental solutions that have been in wide use for the analysis of the infiltration penetration of atmospheric water from the watered land surface and for the assessment of moisture transfer in the aeration zone.

However, this form of the solution is not convenient to use in the studies of infiltration characteristics, such as the rate of infiltration (i) and the accumulation of moisture reserves in the aeration zone (specific accumulated infiltration volume I). This requires one either to use special computational methods, such as iteration methods (Parlange et al. 2002), or to study the asymptotic solutions of the Eq. 2.69, which can be readily obtained in the form of finite analytical expressions, but are valid only for the description of the initial ($t \rightarrow 0$) or, conversely, final and very long infiltration periods ($t \rightarrow \infty$) (see below). Therefore, it is of interest to carry out an additional study of the Green–Ampt solution to obtain analytical relationships describing the behavior of functions $i(t)$ and $I(t)$ in the *explicit* form.

2.1.3.6 Modified and Explicit Forms of the Green–Ampt Model and Formulations for Infiltration Analysis

Rewrite Eqs. 2.68 and 2.69 as (Salvucci and Entekhabi 1994):

$$i = u^w \Delta\theta = k_s \left(1 + \frac{(h_0 + h_f) \Delta\theta}{I} \right), \quad (2.70)$$

$$t = \frac{I}{k_s} - \frac{\Delta\theta(h_0 + h_f)}{k_s} \ln \left(1 + \frac{I}{\Delta\theta(h_0 + h_f)} \right), \quad (2.71)$$

where $i = \frac{dI}{dt}$, $I = \Delta\theta z_f$, $\Delta\theta = \theta_s - \theta^0$ (see Sect. 2.1.3.3). The substitution of function I , determined from the solution (2.70), into (2.71) yields the generalized expression

$$t = \frac{\chi}{\bar{i} - 1} - \chi \ln \left(\frac{\bar{i}}{\bar{i} - 1} \right), \quad \chi = \frac{\Delta\theta(h_0 + h_f)}{k_s} \equiv \frac{S^2}{2k_s^2}, \quad \bar{i} = \frac{i}{k_s} \quad (2.72)$$

relating the process time t with the dimensionless specific discharge, $\bar{i}$; $S^2 = 2k_s \Delta\theta(h_0 + h_f)$.

The solution (2.72) can be differentiated with respect to t , yielding

$$\bar{i}(\bar{i} - 1)^2 + \chi \frac{d\bar{i}}{dt} = 0, \quad (2.73)$$

or, upon the introduction of the new dimensionless variable $\tau = \frac{t}{t + \chi} = \frac{\bar{i}}{1 + \bar{i}}$

$\left(\bar{i} = \frac{t}{\chi} \right)$, we obtain

$$\bar{i}(\bar{i} - 1)^2 + (1 - \tau)^2 \frac{d\bar{i}}{d\tau} = 0. \quad (2.74)$$

Thus, a new representation of the Green–Ampt equation (Salvucci and Entekhabi 1994) in the form of the ordinary differential Eq. 2.74, whose solution must satisfy the boundary condition

$$\bar{i} = \infty \text{ at } \tau = 0 \quad (2.75)$$

(since at $t \rightarrow 0$, $I = 0$ and hence $\bar{i} \rightarrow \infty$).

Next it was proposed to approximate $\bar{i}$ by the power series:

$$\bar{i} \cong A_0 \tau^{-1/2} + A_1 + A_2 \tau^{1/2} + A_3 \tau + \dots + A_n \tau^{(n-1)/2}. \quad (2.76)$$

From physical consideration it is clear that when $\tau = 1$ ($t \rightarrow \infty$), the values of the function $\bar{i}$ must be equal to unity; hence the sum of all coefficients A_n in the series must also be equal to unity. The substitution of (2.76) into the differential Eq. 2.74 and some additional operations allow us to find the coefficients A_n of the Eq. 2.76 whatever the number of terms in the series n . Thus, in the case of a three-term relationship, passing to dimensional variables, we obtain:

$$i(\bar{i}) \cong k_s \left\{ \frac{\sqrt{2}}{2} \left(\frac{\bar{i}}{1+\bar{i}} \right)^{-1/2} + \frac{2}{3} - \frac{\sqrt{2}}{6} \left(\frac{\bar{i}}{1+\bar{i}} \right)^{1/2} + \frac{1-\sqrt{2}}{3} \left(\frac{\bar{i}}{1+\bar{i}} \right) \right\}. \quad (2.77)$$

The Eq. 2.77 can be integrated, allowing one to obtain the expression for the specific accumulated infiltration volume:

$$I(\bar{i}) \cong k_s \chi \left\{ \left(1 - \frac{\sqrt{2}}{3} \right) \bar{i} + \left(\frac{\sqrt{2}}{3} \right) (\bar{i} + \bar{i}^2)^{1/2} + \left(\frac{\sqrt{2}-1}{3} \right) \ln(1+\bar{i}) + \left(\frac{\sqrt{2}}{3} \right) \ln \left(1 + 2\bar{i} + 2(\bar{i} + \bar{i}^2)^{1/2} \right) \right\}. \quad (2.78)$$

Plots in Fig. 2.5 reflect the major features in the behavior of dimensionless functions $\bar{i}(\bar{i})$ and $\bar{I}(\bar{i})$: an abrupt drop in the specific discharge i over time at the initial stages of infiltration and its asymptotic approximation to the limiting value $i = k(\theta_s) \equiv k_s$ during long stages (approximately, when $t > 5S^2/k_s^2$); conversely, $\bar{I}$ is an increasing function, which becomes nearly linear at $\bar{i} > 3 - 5$.

An attractive and productive idea was to transform Green–Ampt equations with the use of Lambert W -function (Barry et al. 1993, 2005; Parlange et al. 2002), defined as

$$We^W = x, \quad x \geq -e^{-1}. \quad (2.79)$$

The graphical representation of function $W = W(x)$ (Fig. 2.6a) has two branches: $W_{-1}(x) \leq -1$ and $W_0(x) \geq -1$ (the domain $W_0(x) \geq 0$ is not considered in this class of problems). In the solution of a real problem, it is advisable to transpose the independent variable (x) into the same part of the equation, representing the latter as

Fig. 2.5 Calculation of the basic infiltration functions: $\bar{i}(\bar{t}) = i/k_s$ (dimensionless instantaneous infiltration capacity) and $\bar{I}(\bar{t}) = I/\chi k_s$ (dimensionless accumulated infiltration) from analytical solutions: 1 – Eqs. 2.77, 2.78; 2 – Eqs. 2.87, 2.88; 3 – Eqs. 2.82, 2.84. $\bar{t} = t/\chi$, $\chi = S^2/2k_s^2$, $A = 2k_s/3$

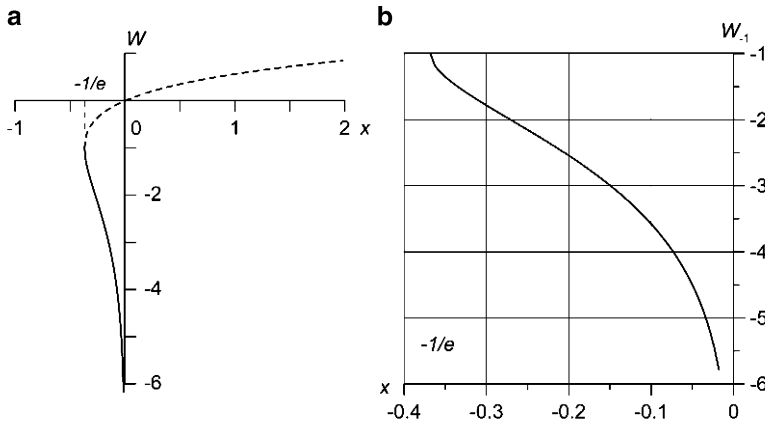
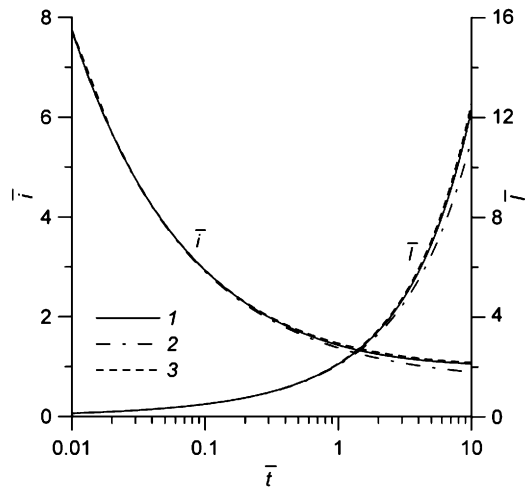


Fig. 2.6 Lambert W -function. (a) Two real branches [$W_0(x)$ (dashed line) and $W_{-1}(x)$ (full line)]; (b) larger scale plot of $W_{-1}(x)$

$y = xe^x$, and consider the inverse function of y ; mathematically, this procedure can be formulated as

$$y = xe^x \leftrightarrow x = W(y). \quad (2.80)$$

Let us represent the Green–Ampt formula (2.69) in the form

$$\bar{I} = \bar{t} + \ln(1 + \bar{I}), \quad (2.81)$$

which can be also written in the equivalent form:

$$-\exp[-(1 + \bar{t})] = -(1 + \bar{I}) \exp[-(1 + \bar{I})]; \quad (2.81a)$$

here $\bar{I} = I/(S^2/2k_s)$, $\bar{t} = t/(S^2/2k_s^2)$, $I = \Delta\theta z_f$, $S = \sqrt{2k_s\Delta\theta(h_0 + h_f)}$. In accordance with Eq. 2.80, $x = -(1 + \bar{I})$, and $y = -\exp[-(1 + \bar{I})]$. From here it follows

$$\bar{I} = -1 - W_{-1}[-\exp(-1 - \bar{t})], \quad (2.82)$$

i.e., we come to the explicit solution of the Green and Ampt problem for dimensionless cumulative infiltration.

For calculations by (2.82), the plot of the function $W_{-1}(x)$ in Fig. 2.6b can be used. Another approach is to use the approximation for the function $W_{-1}(x)$ obtained by a special method (Barry et al. 2005):

$$W_{-1}(x) \approx -1 - \frac{\sigma^2}{2} - \frac{\sigma}{1 + \sigma/6}, \quad (2.83)$$

$\sigma = \sqrt{-2 - 2\ln(-x)}$. This approximation is valid in the range $-1/e \leq x \leq 0$ and has a maximum relative error of 0.47%.

The flux $\bar{i}$ can be calculated directly from (2.82) by the differentiation of (2.83) with respect to $\bar{t}$. The flux $\bar{i}$ can also be calculated using (Barry et al. 1993, 2005):

$$\bar{i} = \frac{W_{-1}[-\exp(-1 - \bar{t})]}{1 + W_{-1}[-\exp(-1 - \bar{t})]}. \quad (2.84)$$

As can be seen from the plot in Fig. 2.5, the solutions of (2.84) and (2.82) almost coincide with the solutions (2.77) and (2.78).

2.1.3.7 Some Generalized Approximations

Analysis of the solutions given above allows us to obtain expressions for studying the limiting regimes of the infiltration penetration of water into initially incompletely saturated shallow sediments.

Thus, at small t , when the moistening front lies near the surface [$z_f/(h_0 + h_f) \ll 1$], the solutions (2.77), (2.78), and (2.82), (2.84) have the asymptotic representations for infiltration capacity and accumulated infiltration:

$$i = \frac{\sqrt{2k_s(h_0 + h_f)\Delta\theta}}{2} \frac{1}{\sqrt{t}}, \quad I = \sqrt{2k_s(h_0 + h_f)\Delta\theta} \sqrt{t}. \quad (2.85)$$

At large time (t), functions i and I asymptotically tend to the limits

$$i = k_s, \quad I = k_s t. \quad (2.86)$$

The analysis given above clarifies the structure of the generalized expressions (Philip 1957b, 1987)

$$I(t) = S\sqrt{t} + At, \quad (2.87)$$

$$i(t) = \frac{dI}{dt} = \frac{1}{2} \frac{S}{\sqrt{t}} + A, \quad (2.88)$$

which are often used for the approximated description of infiltration process. Now the expression

$$S = \sqrt{S_0^2 + S^2(\theta_s, \theta^0)}, \quad (2.89)$$

$$S_0^2 = 2k_s h_0 \Delta\theta, \quad S_0^2(\theta_s, \theta^0) = 2k_s h_f \Delta\theta, \quad \Delta\theta = \theta_s - \theta^0, \quad (2.89a)$$

can be associated with the notion of sorptivity (see Sect. 2.1.3.3) for the case of infiltration from the surface covered by a water layer; $A = (1/3 \div 1)k_s$ is the gravity factor. Note, however, that the solutions (2.87) and (2.88) do not directly follow from the model considered here.

More strict expressions for S , which take into account the features of the retention function can be found in the works (Parlange et al. 1985, 1992; Broadbridge 1990).

Analysis of (2.88) shows that in course of time (tentatively, at $t > t_g = (3S/2k_s)^2$) the effect of the first term, which accounts for the role of capillary-adsorption forces, becomes negligible and the rate of imbibition is determined by hydraulic conductivity of the porous material, i.e., by the second term of the Eq. 2.88, which accounts for the gravity movement of moisture. Most authors recommend using the values of A between $k_s/3$ and $2k_s/3$ for not very long periods.

This range also most often contains the estimates of parameter A by the formula (Haverkamp et al. 1994; Lassabatère et al. 2006):

$$A = k_s \left\{ \frac{(2 - \beta)}{3} \left[1 - \left(\frac{\theta^0}{\theta_s} \right)^n \right] + \left(\frac{\theta^0}{\theta_s} \right)^n \right\}, \quad (2.90)$$

where n is the exponent in the Averjanov formula (2.10) for the moisture transfer coefficient; the empirical coefficient β for most lithologic members at their moisture content $\theta^0 < 0.25\theta_s$ is 0.6.

The plots in Fig. 2.5 show that the approximate solutions (2.87) and (2.88) can be used in practical calculations.

The obtained relationships allow us, by analogy with the Green–Ampt problem, to write the generalized expressions determining the position of the moisture transfer front ($z_f = I/\Delta\theta$):

$$z_f(t) = \xi_f \sqrt{t} + \frac{A}{\Delta\theta} t \text{ at } t \leq t_g, \quad (2.91)$$

$$z_f(t) = \frac{k_s}{\Delta\theta} (t - t_g) + z_f(t_g) \text{ at } t > t_g, \quad (2.92)$$

where parameter $\xi_f = S/\Delta\theta$ accounts for the contribution of capillary forces. It can be seen that the infiltration time is divided into two periods: at times less than t_g , the moisture front propagation velocity is governed by both the gravity and capillary mechanisms, while the gravity moisture transport dominates for time greater than t_g .

Wang et al. (2003) developed an algebraic model for the description of soil water infiltration based on Parlange (1971b) approximation of Richards equation and on soil retention curve (2.6) and hydraulic conductivity Eq. 2.11 given by Brooks and Corey (1964). When the initial soil water content is small and can be approximated

as $\theta_r = \theta^0$ and the boundary condition is $\theta(z = 0, t) = \theta_s$, integrating (2.22) for soil water provides the following four equations (Wang et al. 2003, 2009)

$$\theta - \theta_r = \begin{cases} \left(1 - \frac{z}{z'_f}\right)^\alpha \Delta\theta & z \leq z'_f, \\ 0 & z > z'_f, \end{cases} \quad (2.93)$$

$$i = k_s \left(1 + \frac{1}{\beta z'_f}\right), I = \frac{\Delta\theta}{1 + \alpha} z'_f, t = \frac{\Delta\theta}{(1 + \alpha)k_s} \left(z'_f - \frac{\ln(\beta z'_f + 1)}{\beta}\right), \quad (2.94)$$

where z'_f is the wetting front distance; $\alpha = \lambda/m$ is the comprehensive shape coefficient of the soil water content distribution, which determines the amount of water in a soil profile for a fixed wetting front distance; $\beta = m/a$ (a is a constant) is a soil suction allocation coefficient; i is the infiltration rate; I is the cumulative infiltration; $\Delta\theta = \theta_s - \theta_r$.

It is easy to show that the Wang et al. (2003) algebraic model transforms into the Green–Ampt model if one assumes the following relationships to hold between model characteristics

$$z_f = \frac{z'_f}{1 + \alpha}, h_f = \frac{1}{\beta(1 + \alpha)}. \quad (2.95)$$

Formulas (2.77), (2.78), (2.87), (2.88), (2.94) and similar relationships (Ravi and Williams 1998; Williams et al. 1998) are intended for adapting the theoretical models to the regularities observed in atmospheric water infiltration from the land surface (Chahinian et al. 2005). Since infiltration is a component of the general water balance equation for hydrological basins, the relationships presented above give formulations for runoff-infiltration analysis (Sect. 10.7).

2.1.3.8 Traveling Wave Solution of the Richards Equation

We consider vertical infiltration into initially wet porous medium domain, $\theta(z, 0) = \theta^0$. Pore water moves from $z = -\infty$ to $z = +\infty$. Suppose that the nonlinearity of the process ensures the balance between the gravity and diffusion components of moisture flux, resulting in that a stationary (in moving coordinates) moisture wave ($\theta^0 < \theta < \theta_0$) forms during long-time infiltration (theoretically, at $t \rightarrow \infty$), which moves with nearly constant velocity u^w , where $\theta = \theta_0$ at $z = -\infty$ and $\theta = \theta^0$ at $z = +\infty$.

Multiplying the original Eq. 2.22 by $\partial z / \partial \theta$ with a change $z = -z$ (in this case, the z -axis will be directed vertically downward) we obtain (Youngs 1957)

$$-\frac{\partial z}{\partial t} = \frac{\partial}{\partial \theta} \left(D(\theta) \frac{\partial \theta}{\partial z} \right) - \frac{\partial k(\theta)}{\partial \theta}. \quad (2.96)$$

In this representation of moisture transfer equation, the function $z = z(\theta, t)$ is the space coordinate of the point where the moisture content in moment t is θ .

The assumption that the moisture front moves in the vertical direction with a constant velocity allows us to write the identity

$$\frac{\partial z}{\partial t} = \frac{k(\theta_0) - k(\theta^0)}{\theta_0 - \theta^0} = u^w = \text{const}, \quad (2.97)$$

where $k(\theta_0)$ and $k(\theta^0)$ are the values of unsaturated hydraulic conductivity at $\theta = \theta_0$ and $\theta = \theta^0$. Now the Eq. 2.96 becomes

$$-\frac{d}{d\theta} \left(D(\theta) \frac{d\theta}{dz} \right) + \frac{dk(\theta)}{d\theta} = \frac{k(\theta_0) - k(\theta^0)}{\theta_0 - \theta^0}. \quad (2.98)$$

Integrating (2.98) from θ to θ_0 yields

$$D(\theta) \frac{d\theta}{dz} + (k(\theta_0) - k(\theta)) = (k(\theta_0) - k(\theta^0)) \frac{\theta_0 - \theta}{\theta_0 - \theta^0}. \quad (2.99)$$

Eq. 2.99 can be solved by separation of variables, yielding

$$(\theta_0 - \theta^0) \int_{\theta^0}^{\theta} \frac{D(\theta)}{k(\theta)(\theta_0 - \theta^0) - k(\theta^0)(\theta_0 - \theta) - k(\theta_0)(\theta - \theta^0)} d\theta = z(\theta) - z_f, \quad (2.100)$$

where $z_f = z(\theta^0) = u^w t$ is the position of the leading edge of the moisture wave. The solution (2.100) of the moisture transfer equation can also be obtained by direct transformation of the initial Eq. 2.23 with the substitution (2.46) (Philip 1957c; Ross and Parlange 1994; Witelski 2005).

Formally speaking, we have come to a solution of the traveling-wave type (2.46). This solution has a self-similar front moving at a velocity of u^w without changing its shape. Theoretically, the wave front length is infinite, stretching from $z = -\infty$ where $\theta = \theta_0$ to $z = +\infty$ where $\theta = \theta^0$ at any given time. To make this solution of practical value, Zlotnik et al. (2007) suggested to consider $(\theta_0)^* = \theta_0 - \Delta_0$ and $(\theta^0)^* = \theta^0 - \Delta^0$ (Δ_0 and Δ^0 are small positive values) to avoid integrand singularities at both integration limits $\theta = \theta_0$ and $\theta = \theta^0$. Zlotnik et al. (2007) showed also that the solution (2.100) allows generating different exact solutions for infiltration problems for arbitrary finite time and can be a good benchmark for the verification of the accuracy of solution methods for transient flow conditions.

The solution (2.100) can be represented in a closed form given the analytical functions $D(\theta)$ and $k(\theta)$. Thus, for the Averjanov–Gardner moisture transfer model (2.10, 2.15) in the case of infiltration into relatively dry shallow sediments ($\theta^0 = \theta_r$) at $k(\theta_r) = 0$ we obtain:

$$\frac{\beta}{\alpha} \int_0^{\tilde{\theta}} \frac{\tilde{\theta}^{n-1}}{\tilde{\theta}^n - \tilde{\theta}} d\tilde{\theta} = z(\tilde{\theta}) - u^w t, \quad (2.101)$$

where

$$\tilde{\theta} = \frac{\theta - \theta_r}{\theta_0 - \theta_r}, \quad \beta = \frac{\theta_s - \theta_r}{\theta_0 - \theta_r}, \quad u^w = \frac{k(\theta_0)}{\theta_0 - \theta_r} = \frac{k_s}{\beta^{n-1} \Delta\theta}, \quad \Delta\theta = \theta_s - \theta_r. \quad (2.101a)$$

Integrating (2.101) we obtain the solution of the problem in the explicit form:

$$\tilde{\theta}(\eta) = \left(1 - e^{(n-1)\alpha\eta/\beta}\right)^{\frac{1}{n-1}}. \quad (2.102)$$

If the soil is not initially dry and has a nonuniform initial distribution of water content then the motion of the wetting front will change due to the interaction of the infiltration flow with the pre-existing soil condition (Witelski 2005). Approximate solutions for this situation were derived by Witelski (2005) who suggested a simple procedure for scaling the wetting front advancing into a soil layer with heterogeneous initial water content profile.

2.2 On Models Coupling Water Infiltration and Solute Transport

Unsaturated flow forms as the result of infiltration of precipitation (during rains or snow melting); infiltration from a surface water body underlain by a low-permeability bed (or clayey bottom sediments); or a short-time waterlogging of land surface as the result of accidental spills of liquids (solutions) with different composition. In all cases, the infiltration water can deliver into the subsurface hydrosphere some pollutants whose fate can be predicted by solving migration problems of a specific class.

The mathematical formalization of the transport of chemical components dissolved in infiltration water requires the joint solution of Richards equations describing moisture transfer in the aeration zone and the continuity equation for the mass flux of the matter. Thus, the unsteady process in three-dimensional space following Eq. 2.24 can be described by the mass transfer equation

$$\frac{\partial \theta C}{\partial t} - \nabla \cdot (\mathbf{D} \cdot \nabla C - \mathbf{q} C) = 0. \quad (2.103)$$

However, most hydrogeological problems arising from area-distributed pollution of infiltration water are solved in one-dimensional vertical formulation, which will be the focus of the analysis below (Sects. 2.2.1 and 2.2.2). As was the case with the analysis of mass transfer in aquifers, we will successively consider two calculation schemes (models): a purely advective scheme, when the dispersion of solutes in the porous medium is neglected, and an advection–dispersion one, taking into account the effect of longitudinal dispersion because of fluctuations in flow velocities in pores.

The actual heterogeneity of the near-surface sediments largely limits the use of simplified one-dimensional models, requiring the description of macrodispersion effects, which goes beyond the scope of this work.

2.2.1 Advection: A Characteristic Solution

As the first step, we consider a system of moisture and mass transfer equations without regard for dispersion effects, which has the following form:

$$\frac{\partial \theta}{\partial t} + \frac{\partial q}{\partial z} + W_f = 0, \quad (2.104)$$

$$\frac{\partial}{\partial t}(\theta C) + \frac{\partial}{\partial z}(qC) + W_s = 0; \quad (2.105)$$

here W_f and W_s are functions accounting for the effect of distributed (three-dimensional) sources–sinks of moisture and solute.

Differentiating the first and second terms of Eq. 2.105 and regrouping the partial derivatives of functions θ , q and C , we obtain

$$\theta \frac{\partial C}{\partial t} + q \frac{\partial C}{\partial z} + C \left(\frac{\partial \theta}{\partial t} + \frac{\partial q}{\partial z} \right) + W_s = 0. \quad (2.106)$$

The comparison of (2.106) and (2.104) shows that the expression in the parentheses in (2.106) corresponds to $-W_f$. Thus, the system of equations can be transformed into the single equation:

$$\theta \frac{\partial C}{\partial t} + q \frac{\partial C}{\partial z} = CW_f - W_s; \quad (2.107)$$

here, in the general case, $\theta = \theta(z, t)$ and $q = q(z, t)$, the z -axis is directed vertically downward.

Let us restrict our consideration to the migration process in a homogeneous medium, assuming $W_f = 0$ and $W_s = 0$, to obtain

$$\theta \frac{\partial C}{\partial t} + q \frac{\partial C}{\partial z} = 0. \quad (2.108)$$

The partial differential Eq. 2.108 corresponds to the system of first-order ordinary differential equations

$$\frac{dt}{\theta} = \frac{dz}{q} = \frac{dC}{0}, \quad (2.109)$$

which are referred to as characteristic. From here, in particular, we obtain the equality

$$\theta(z, t)dz - q(z, t)dt = 0. \quad (2.110)$$

The left part of (2.110) is the total differential of some function $\eta(z, t)$, i.e.

$$q(z, t)dt - \theta(z, t)dz = d\eta(z, t). \quad (2.111)$$

Since

$$d\eta = \frac{\partial \eta}{\partial t} dt + \frac{\partial \eta}{\partial z} dz, \quad (2.112)$$

this is equivalent to

$$\theta = \frac{\partial \eta}{\partial z}, \quad q = -\frac{\partial \eta}{\partial t}. \quad (2.113)$$

From here it follows that the function $\eta(z, t)$, relating the parameters of the initial Eq. 2.108, reflects the dynamics of the frontal moisture transfer in the aeration zone. To determine it, we write the equation in total differentials as:

$$d\eta = 0. \quad (2.114)$$

The general solution of the Eq. 2.114 has the form

$$\eta(z, t) = c, \quad (2.115)$$

i.e., the function η is the integral of (2.110), c is a constant.

The first equations (2.113) is satisfied by the function

$$\eta(z, t) = \int_{z_0}^z \theta(z, t)dz + \varphi(t), \quad (2.116)$$

where $\varphi(t)$ is an arbitrary function of t ; z_0 is an arbitrary point on the coordinate axis; in this problem it corresponds to the position of the front in the initial moment (t_0). We choose the function $\varphi(t)$ to satisfy the second equality (2.113), i.e.,

$$\frac{\partial \eta}{\partial t} = \frac{\partial}{\partial t} \int_{z_0}^z \theta(z, t)dz + \varphi'(t) = -q(z, t), \quad (2.117)$$

or

$$\int_{z_0}^z \frac{\partial \theta(z, t)}{\partial t} dz + \varphi'(t) = -q(z, t). \quad (2.118)$$

By using the original equality (2.108), we rewrite Eq 2.118. as

$$-\int_{z_0}^z \frac{\partial q(z, t)}{\partial z} dz + \varphi'(t) = -q(z, t). \quad (2.119)$$

Integration yields

$$-q(z, t) + q(z_0, t) + \varphi'(t) = -q(z, t), \quad (2.120)$$

whence

$$\varphi'(t) = -q(z_0, t), \quad (2.121)$$

and hence

$$\varphi(t) = -\int_{t_0}^t q(z_0, t) dt + c', \quad (2.122)$$

where c' is an arbitrary constant, which, with appropriately chosen initial conditions z_0, t_0 , can be taken to be zero.

Thus, the integral function $\eta(z, t)$ (2.113) can be written as:

$$\eta(z, t) = \int_{z_0}^z \theta(z, t) dz - \int_{t_0}^t q(z_0, t) dt. \quad (2.123)$$

With $q(z, t)$ taken as the initial function for calculating the general integral (the second formula in 2.113), we come to another integral formula equivalent to (2.123):

$$\eta(z, t) = \int_{z_0}^z \theta(z, t_0) dz - \int_{t_0}^t q(z, t) dt. \quad (2.124)$$

The equalities (2.123)–(2.124) with the additional condition

$$dC(\eta) = 0, \text{ or } C = \text{const along the characteristic } \eta(\theta, t), \quad (2.125)$$

following from (2.109), can be regarded as the generalized characteristic solution of the problem (2.108). This solution implies that the solute concentration does not change along the characteristic $\eta(z, t)$.

Analysis of (2.123) allows us to come to useful physical conclusions. Physically, $\eta(z, t)$ could be thought of as a moving spatial coordinate in relation to a solute front that was located at the point $z = z_0$ at time $t = t_0$ (Wilson and Gelhar 1981; Nachabe et al. 1995). The location of the solute front $z = z_f(t)$ can be determined by setting $\eta = 0$. The condition $\eta > 0$ corresponds to points located ahead of the front, while $\eta < 0$ corresponds to points behind the front. The first term on the right-hand side of the characteristic (2.123) represents the cumulative change in water content, $U(z, t)$, between z and z_0 ,

$$U(z, t) = \int_{z_0}^z \theta(z, t) dz. \quad (2.126)$$

The second term is the cumulative volumetric water infiltrated at the section $z = z_0$ between time t and t_0 :

$$V(t) = \int_{t_0}^t q(z_0, t) dt. \quad (2.127)$$

Therefore, the characteristic solution can be written as (Wilson and Gelhar 1981):

$$\eta(z, t) = U(z, t) - V(t), \quad (2.128)$$

and the position of the concentration front is determined by the equality

$$U(z, t) = V(t). \quad (2.129)$$

Let us give some graphic illustration to the obtained result (Fig. 2.7). Suppose that a volume $V(t)$ of water containing some indicator solute in concentration C_0 entered the aeration zone within time interval $t - t_0$, resulting in a change in the moisture content profile as shown in Fig. 2.7 (the shaded area). The position of the concentration front z_f (the wavy line in Fig. 2.7) is determined by (2.128) at $\eta = 0$. Since $U(z_f) = V$, the area of the domain $z_0 < z < z_f$ (shown by dots in Fig. 2.7), where $C = C_0$, must be equal to the shaded area. From here it follows that the vertical displacement velocity of the solute front in the incomplete-saturation zone is always less than the velocity of the moisture front. Physically, this phenomenon can be explained by the fact that during the motion of the solute, the transport process involves all water contained in the pores, $\theta(z, t)$, while the propagation dynamics of the moisture front is controlled only by an increase in moisture content, which is equal to the difference between the current value of the volumetric moisture content of the subsurface material, $\theta(z, t)$, and the initial moisture content, $\theta(z, t_0)$. The velocity of the concentration front is determined by the dynamics of moisture distribution, however the concentration behind the transport front, C_0 , in the absence of dispersion, remains unchanged.

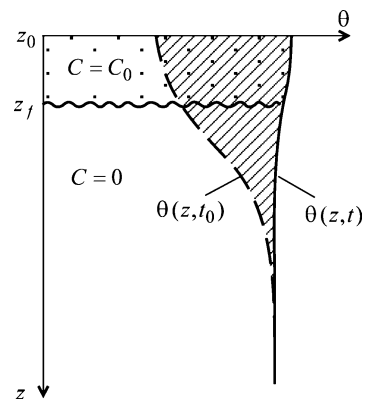


Fig. 2.7 Relative rates of movement of moisture and solute during transient infiltration (Wilson and Gelhar 1981). Explanations see in the text (Reproduced according to terms of use of licensed materials of American Geophysical Union, AGU)

From this viewpoint it is clear that, when the initial moisture distribution is not uniform, the thickness of the concentration parcel that forms during polluted water input into the aeration zone within a limited time interval will vary in the process of water infiltration from the surface. Thus, when moisture content increases with depth, for the solute balance to hold, the thickness of the layer of originally polluted water must decrease. The picture will be inverse if the moisture content decreases with depth. Nachabe et al. (1995) used a relationship (2.123) (assuming $t_0 = 0$ and $z_0 = 0$) to determine the coordinate η of the solute front exactly using the parametric flow solution for $\theta(z, t)$ -function obtained earlier by Broadbridge and White (1988).

To determine the position of the concentration front in the case of constant infiltration rate q through the aeration zone with steady-state moisture profile $\theta(z)$, one can use the first solution of the initial characteristic Eq. 2.108 in the form (2.123):

$$qt = \int_0^z \theta(z) dz, \quad (2.130)$$

with the assumption that $t_0 = 0$, $z_0 = 0$. The propagation velocity of the concentration front is (Vanderborght et al. 2000a):

$$u(z) = \frac{qz}{\int_0^z \theta(z) dz}. \quad (2.130a)$$

From general physical considerations it is clear that the moistening front running appreciably ahead of the concentration front provides conditions for solute migration (with the infiltration rate $q = \text{const}$) under quasisteady conditions in terms of the moisture regime. If the moisture function behind the moistening front is steady, and the values of θ vary over depth only slightly, the formula (2.130) yields

$$u = \frac{q}{\bar{\theta}}, \quad (2.131)$$

where, in the problems on the regional scale, $\bar{\theta}$ is identified with the value of mean rock moisture content that has formed under infiltration recharge of groundwater.

In some cases, the assumption that the moisture motion is steady allows us to find the distribution $\theta(z)$ in the explicit form thus obtaining an expression describing the displacement of the concentration in a closed analytical form.

2.2.2 Dispersion During Adsorption of Water by Soil

2.2.2.1 A General Solution

As well as in Sect. 2.1.3.3, we consider here a limiting case of moisture imbibition by soil (2.132), when the gravity effect may be neglected

$$\frac{\partial \bar{\theta}}{\partial t} = \frac{\partial}{\partial z} \bar{q}(\bar{\theta}), \quad \bar{q}(\bar{\theta}) = -D(\bar{\theta}) \frac{\partial \bar{\theta}}{\partial z}, \quad (2.132)$$

which is true in the first moments of infiltration; the normalized specific flux, $\bar{q}$, is determined by $\bar{q}(\bar{\theta}) = q/\Delta\theta$, $\bar{\theta} = (\theta - \theta^0)/\Delta\theta$, $\Delta\theta = \theta_s - \theta^0$. In this case, Eq. 2.103 becomes

$$\left(\bar{\theta} + \frac{\theta^0}{\Delta\theta}\right) \frac{\partial \bar{C}}{\partial t} - D(\bar{\theta}) \frac{\partial \bar{\theta}}{\partial z} \frac{\partial \bar{C}}{\partial z} - \frac{\partial}{\partial z} \left[D_s \left(\bar{\theta} + \frac{\theta^0}{\Delta\theta} \right) \frac{\partial \bar{C}}{\partial z} \right] = 0. \quad (2.133)$$

One may assume that both $\bar{\theta}$ and $\bar{C}$ profiles preserve similarity in terms of the Boltzmann variable $\lambda = z/\sqrt{t}$. With $\lambda = z/\sqrt{t}$ (Smiles et al. 1978) (2.132) and (2.133) become respectively (Smiles et al. 1978; Gandola et al. 2001)

$$\frac{\lambda}{2} \frac{d\bar{\theta}}{d\lambda} + \frac{d}{d\lambda} \left(D(\bar{\theta}) \frac{d\bar{\theta}}{d\lambda} \right) = 0, \quad (2.134)$$

$$\frac{d}{d\lambda} \left(D'_s(\bar{\theta}) \frac{d\bar{C}}{d\lambda} \right) + \frac{G(\lambda)}{2} \frac{d\bar{C}}{d\lambda} = 0; \quad (2.135)$$

here $\bar{C} = (C - C^0)/(C_s - C^0)$; D_s is the coefficient of dispersion, $D'_s = \theta D_s$,

$$G(\lambda) = \left(\bar{\theta} + \frac{\theta^0}{\Delta\theta} \right) \lambda + 2D(\bar{\theta}) \frac{d\bar{\theta}}{d\lambda} = \left(\bar{\theta} + \frac{\theta^0}{\Delta\theta} \right) \lambda - \int_0^{\bar{\theta}} \lambda du. \quad (2.136)$$

A solution to (2.134) and (2.135) is sought subject to the boundary condition: $\bar{\theta} = \bar{C} = 1$ at $\lambda = 0$, and $\bar{\theta} = \bar{C} = 0$ as $\lambda \rightarrow \infty$.

Equation (2.135) may be written as the linear equation

$$\frac{d}{d\lambda} \left(D'_s(\lambda) \frac{d\bar{C}}{d\lambda} \right) + \frac{G(\lambda)}{2} \frac{d\bar{C}}{d\lambda} = 0. \quad (2.137)$$

The substitution $V = D'_s(\lambda) d\bar{C}/d\lambda$ results in the equation

$$\frac{dV}{d\lambda} + \frac{G(\lambda)}{2D'_s(\lambda)} V = 0. \quad (2.138)$$

Integration of (2.138) yields

$$V = V_0 \exp \left[-\frac{1}{2} \int_0^{\lambda} G(\lambda) \frac{d\lambda}{D'_s(\lambda)} \right]. \quad (2.139)$$

It then follows (Smiles et al. 1978)

$$\bar{C} = 1 - \frac{M(\lambda)}{M(\infty)}, \quad (2.140)$$

in which

$$M(\lambda) = \int_0^\lambda \left\{ \frac{1}{D'_s(\lambda)} \exp \left[-\frac{1}{2} \int_0^\lambda \frac{d\lambda}{D'_s(\lambda)} \right] \right\} d\lambda. \quad (2.140a)$$

If $D'_s(\theta)$ is known, the calculation of $D'_s(\lambda)$ is straightforward since $\theta(\lambda)$ is unique.

2.2.2.2 Derivation of a Particular Solution

Suppose that the moisture profile in the porous medium can be described by the equation:

$$\bar{\theta} = (1 - \bar{\lambda})^{1/N}, \quad (2.141)$$

where $\bar{\theta} = (\theta - \theta_r)/\Delta\theta$, $\Delta\theta = \theta_s - \theta_r$, meaning that the moisture transfer during infiltration into the shallow sediment is considered for the initial moisture content of $\theta^0 = \theta_r$; $\bar{\lambda} = \lambda/\lambda_f$; $\lambda = z/\sqrt{t}$; λ_f is a variable characterizing the position of the moistening front z_f at fixed t ($\lambda_f = z_f/\sqrt{t}$); $N > 1$. A moisture profile described by a power function similar to (2.141) was considered in works [Gandola et al. \(2001\)](#) and [Wang et al. \(2003, 2009\)](#). In this case, the expression for the diffusivity coefficient (2.38) becomes

$$D(\bar{\theta}) = \frac{\lambda_f^2}{2} N \left(\bar{\theta}^N - \frac{1}{N+1} \bar{\theta}^{2N} \right) \approx \frac{\lambda_f^2}{2} N \bar{\theta}^N. \quad (2.142)$$

Comparing this expression with the first formula (2.15), following from the model of Averjanov and Gardner (2.5), (2.10), we obtain

$$\lambda_f^2 = \frac{2k_s}{\Delta\theta\alpha(n-1)}, N = n-1, \Delta\theta = \theta_s - \theta_r. \quad (2.143)$$

With $h_f = 1/\alpha(n-1)$, $h_0 = 0$ in the expression (2.89) for sorptivity, we obtain

$$\lambda_f = \frac{S(\theta_s, \theta_r)}{\Delta\theta}, \quad (2.143a)$$

i.e., we have the exact equality $z_f = S(\theta_s, \theta_r)\sqrt{t}/\Delta\theta$, which is in agreement with (2.91) at $t/t_g \ll 1$.

In the simplest case of $D'_s = D_s^0 = \text{const}$, the initial Eq. 2.135 becomes

$$\frac{d^2\bar{C}}{d\bar{\lambda}^2} - \frac{\text{Pe}}{2} g(\bar{\lambda}) \frac{d\bar{C}}{d\bar{\lambda}} = 0, \quad (2.144)$$

where $g(\bar{\lambda}) = (1 - \bar{\lambda})^m - \bar{\theta}^0$, $\bar{\theta}^0 = \theta_r/\Delta\theta$, $m = n/(n-1)$, $\text{Pe} = \lambda_f^2/D_s^0$ (an analogue of the Peclet number). The solution of this equation in the segment $0 \leq \bar{\lambda} \leq 1$ has the form:

$$\bar{C} = 1 - \frac{M(\bar{\lambda})}{M(1)}, \quad (2.145)$$

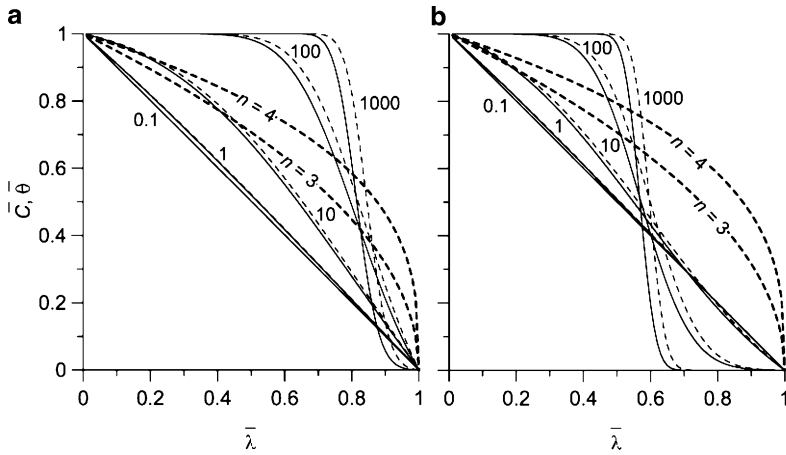


Fig. 2.8 Plots of functions $\bar{C}(\bar{\lambda})$ (full lines for $n = 3$ and thin dashed lines for $n = 4$) and $\bar{\theta}(\bar{\lambda})$ (heavy dashed lines). (a) $\bar{\theta}^0 = 0.1$, (b) $\bar{\theta}^0 = 0.5$. Numbers at curves are the values of parameter Pe

where

$$M(\bar{\lambda}) = \int_0^{\bar{\lambda}} \exp \left[-\frac{Pe}{2} \left(\frac{((1-\bar{\lambda})^{m+1} - 1)}{(m+1)} + \frac{\bar{\theta}^0 \bar{\lambda}^2}{2} \right) \right] d\bar{\lambda}. \quad (2.146)$$

Figure 2.8 gives plots of the solution (2.145), drawn for characteristic values of parameters. Analysis of these plots leads to several useful conclusions regarding the physics of the process: (1) the front of solute lags behind of the moisture front, and this lag is the longer, the greater the value of parameter $\bar{\theta}^0$, characterizing the system capacity; (2) an increase in parameter Pe (a decrease in the dispersion coefficient) causes the compression of concentration fronts (a decrease in the dispersion zone); (3) the shape of the concentration profile features low sensitivity to n .

2.2.3 Advection–Dispersion Transport

Microdispersion of the solute in the unsaturated zone can be described by Eq. 2.103, which in the one-dimensional case becomes

$$\frac{\partial}{\partial t}(\theta C) + \frac{\partial}{\partial z}(qC) - \frac{\partial}{\partial z} \left(D' \frac{\partial C}{\partial z} \right) = 0, \quad (2.147)$$

where $D' = D\theta$ is the longitudinal dispersion coefficient. As was the case with the advection mass transfer, the Eq. 2.147 can be combined with the moisture transport Eq. 2.104. With $W_f = 0$ and $W_s = 0$, we obtain

$$\theta(z, t) \frac{\partial C}{\partial t} + q(z, t) \frac{\partial C}{\partial z} - \frac{\partial}{\partial z} \left(D'(z, t) \frac{\partial C}{\partial z} \right) = 0. \quad (2.148)$$

The majority of approximate solutions of the Eq. 2.148 are based on the assumption that the coefficients q and D near the front vary only slightly over the depth but are functions of time. In this case, the Eq. 2.148 can be written as

$$\frac{\partial C}{\partial t} + u(z, t) \frac{\partial C}{\partial z} - D(z, t) \frac{\partial^2 C}{\partial z^2} = 0, \quad (2.149)$$

where $u(z, t) = q(z, t)/\theta(z, t)$.

We assume that the Eq. 2.149 can describe solute dispersion near the front, whose coordinate $\xi(t)$ in any time t is determined by the characteristic Eq. 2.124, rewritten as

$$\int_0^{\xi(t)} \theta(z, t=0) dz = \int_0^t q[\xi(t), \tau] d\tau, \quad (2.150)$$

i.e., $\xi(t)$ is a variable coordinate characterizing the penetration depth of the piston-like concentration front (Vanderborgh et al. 2000b). From Eq. 2.150, we have

$$\frac{d\xi(t)}{dt} = \frac{q[\xi(t)]}{\theta[\xi(t)]}. \quad (2.151)$$

Let us express t in (2.149) in terms of $\xi = \xi(t)$, assuming $u(z, t) = u(\xi)$ and $D(z, t) = D(\xi)$. We obtain

$$\frac{\partial C}{\partial \xi} + \frac{\partial C}{\partial z} - \frac{D(\xi)}{u(\xi)} \frac{\partial^2 C}{\partial z^2} = 0. \quad (2.152)$$

If the linear relationship $D = \delta_L u$ is valid, then (2.152) becomes the advection–dispersion equation with constant coefficients

$$\frac{\partial C}{\partial \xi} + \frac{\partial C}{\partial z} - \delta_L \frac{\partial^2 C}{\partial z^2} = 0, \quad (2.153)$$

where $\xi = \xi(t)$ serves as the space coordinate of the piston-like displacement front. An approximate solution of (2.153) can be written as

$$\bar{C} = \frac{1}{2} \operatorname{erfc} \frac{z - \xi(t)}{\sqrt{4\delta_L \xi(t)}}, \quad (2.154)$$

similar to Eq. 1.96.

The time coordinate t can be replaced by another cumulative coordinate (Vanderborgh et al. 2000b):

$$I(z, t) = \int_0^t q(z, t) dt; \quad (2.155)$$

here $q(z, t)$ is the velocity (specific rate of infiltration) at depth z in moment t .

The Eq. 2.149 for function $C(I)$ with $\theta = \theta(z)$ and $q = q(t)$ (when the moisture content does not depend on the time coordinate, while the velocity does not depend on the space coordinate) becomes

$$\frac{\partial C}{\partial I} + \frac{1}{\theta(z, 0)} \frac{\partial C}{\partial z} - \frac{\delta_L}{\theta(z, 0)} \frac{\partial^2 C}{\partial z^2} = 0. \quad (2.156)$$

With $\delta_L = 0$, the solution (2.156) yields the position of the piston-like displacement front

$$I(z, t) = \int_0^z \theta(z, 0) dz, \quad (2.157)$$

where $\theta(z, 0)$ is moisture distribution in the aeration zone in the initial moment $t = 0$. If $\theta(z, 0) = \theta = \text{const}$, the solution of the advection–dispersion Eq. 2.156 becomes

$$\bar{C} = \frac{1}{2} \text{erfc} \frac{z\theta - I}{\sqrt{4\delta_L I \theta}}. \quad (2.158)$$

If the moisture content varies over depth, $\theta = \theta(z)$, the function $C(I)$ can be described by expression (2.158) with θ replaced by $\bar{\theta}$:

$$\bar{\theta} = \int_0^z \theta(z, t) dz. \quad (2.159)$$

Finally, it is worth mentioning that the dispersion of solutes in unsaturated sub-surface material has some specific features. As it was shown by experiments (Padilla et al. 1999), the dispersion coefficient in incompletely saturated porous media is greater than that in the same sediments when completely saturated. The general structure of the dispersion coefficient is $D = \zeta_L(\theta_m)u^n$, where the exponent can reach 1.5; θ_m is the volumetric moisture content of flow-through pores. This difference is due to the relatively large volume of stagnant pores (zones) as compared with completely saturated media. Solute exchange between the active pores, through which it is transported, and the stagnant pores is slow. However, from the practical viewpoint, such specification is not fundamental, and the analytical solutions given above are well suited for the analysis of the significance of microdispersion effects.

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Part II

Conceptual Models for Regional Assessment of Solute Transport (Under Homogeneous Liquid Flow Conditions)

The problems that arise in the context of assessing the advective and advection–dispersion transport under near-real conditions can be divided into two large groups. The first group, discussed in this part, deals with studying solute propagation in regional groundwater flows, which commonly feature weak planar variations in flow velocities, as is typical of areas remote from powerful sources (primarily, wells) of concentrated hydrodynamic impact on the aquifer. This is the case when a regional groundwater flow system may be considered as unilateral (one-dimensional). Furthermore, on a regional scale, where the vertical to horizontal dimension ratios are very small, the vertical resistance to groundwater flow may be neglected (the Dupuit–Forchheimer assumption). This allows the migration processes to be studied (a) in a quasi-one-dimensional formulation, allowing solute concentration to be averaged over the aquifer cross-section (see Chap. 3); (b) in a simplified two-dimensional profile formulation, allowing the formation of heterogeneous concentration profiles to be described (see Chaps. 4 and 5).

The solution of appropriate mass-transfer problems can be of use, for example, for studying groundwater pollution under the effect of the so-called non-point source pollution, as well as for the interpretation of data of groundwater isotopic dating. In the mathematical formulation of problems of this type, area-distributed infiltration should be taken into account, while the dispersion component of the mass flux can be neglected, unless macrodispersion is involved, owing to macro-scale heterogeneity in rock permeability or rock dual porosity (see Chap. 6).

The second group of problems, describing the migration in heavily deformed groundwater flows formed by extraction or/and injection wells, will be considered in separate sections (see Part III).

Chapter 3

One-Dimensional Hydrodynamic Mixing Models for Regional Flow Systems Under Areal Recharge Conditions and Their Application to the Interpretation of Isotopic Data

The *regional solute transport problems* considered below are related mostly to the infiltration-type nonpoint-source pollution of the subsurface environment. Nonpoint-sources are the leading cause of groundwater contamination in many rural areas with well-developed agricultural activity. On the other hand, infiltration (groundwater recharge) is considered as a physical process that may contribute to *natural attenuation*. Coupling recharge and aquifer flow characteristics creates a basis for the use of isotope data analysis for groundwater dating.

Conceptualization of water flow and solute transport processes results in simplified planar quasi-one-dimensional models: dissolved chemicals or isotopes are assumed to rapidly distribute over the entire aquifer thickness (i.e., concentration profiles become more level). The resulting analytical solutions are also mostly applicable to the analysis of infiltration-type pollution, yielding heterogeneous solute distributions over aquifer profile, if the sampling system (e.g., a pumping well, whose inflow is determined by the overall aquifer transmissivity) facilitates concentration averaging.

In the case of one-dimensional groundwater flow, determined by water inlet flux, $Q_0[\text{L}^2\text{T}^{-1}]$, at the boundary $x = 0$ of the aquifer and the area-distributed groundwater recharge with the specific rate, $\varepsilon [\text{LT}^{-1}]$, (Fig. 3.1a), flow discharge in an arbitrary section, $Q_x = q_x m$ (a confined aquifer), is the sum of these two components of groundwater flow balance:

$$Q_x = Q_0 + \varepsilon x. \quad (3.1)$$

Now groundwater flow rate (specific discharge) is also a function of coordinate, x :

$$q_x = q_0 + \frac{\varepsilon}{m}x \quad (q_0 = Q_0/m), \quad (3.1a)$$

where m is aquifer thickness [L].

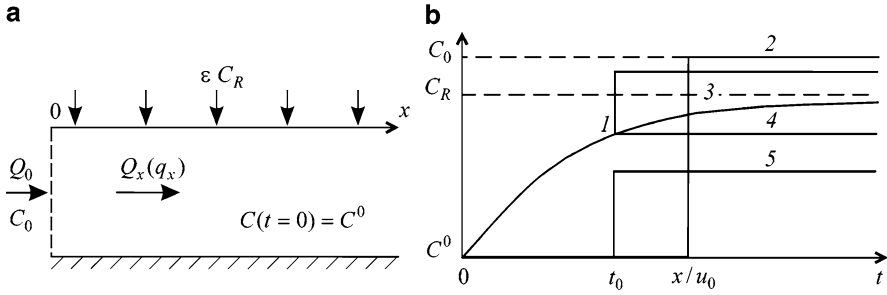


Fig. 3.1 (a) Conceptual scheme of solute migration in a one-dimensional confined flow and (b) the shape of concentration curves. (1) General solution (3.7/3.9), (2) $\varepsilon = 0$, (3) $q_0 = 0$, (4) $C_0 = 0$, (5) $C_R = 0$

Next, in accordance with the integral relationship (1.49), we evaluate the migration time t_0 , required for the water front with concentration C_0 at the input boundary to reach the point x :

$$t_0 = \int_0^x \frac{\phi dx}{q_x} = \frac{1}{\varepsilon^*} \int_0^x \frac{dx}{(x + u_0/\varepsilon^*)} = \frac{1}{\varepsilon^*} \ln \left(1 + \frac{\varepsilon^*}{u_0} x \right), \quad (3.2)$$

where $u_0 = \frac{q_0}{\phi}$, $\varepsilon^* = \frac{\varepsilon}{m\phi}$, ϕ is the aquifer material porosity [$L^3 L^{-3}$].

As was already mentioned, in our consideration the aquifer is viewed as an ideal mixer. This approach to model development allows us to neglect the vertical flow velocity component and the real (nonuniform) concentration distribution over the aquifer thickness using the average concentration profile concept.

3.1 Stable Component Migration

3.1.1 Flow and Mass Balance Under Confined Flow Conditions

Solute balance in the well-mixed aquifer with precipitation-recharged groundwater is described by Eq. 1.12 with

$$W_f \equiv W_f^\varepsilon = -\varepsilon/m, \quad W_s \equiv W_s^\varepsilon = -\varepsilon C_R/m \quad (3.3)$$

(C_R is solute concentration in the infiltration water), which in the one-dimensional case becomes

$$\phi \frac{\partial C}{\partial t} + q_x \frac{\partial C}{\partial x} = \frac{\varepsilon}{m} (C_R - C), \quad (3.4)$$

where $C = C(x, t)$ is the cross-section average concentration in the aquifer at point x at time t . Equation 3.4 is a specific case of the general continuity equation

considered in the theory of kinematic waves (Singh 2002, p. 705). The model (3.4), implying the use of concentrations averaged over the aquifer thickness, is also referred to as *ideal mixing* model.

Substituting into (3.4) the expression for velocity q_x from (3.1a) and replacing C by $C_R - C'$ ($C' = C_R - C$), we obtain

$$\frac{\partial C'}{\partial t} + \varepsilon^* C' + (u_0 + \varepsilon^* x) \frac{\partial C'}{\partial x} = 0. \quad (3.4a)$$

The spatial coordinate x in formula (3.4a) can be related to the time t_0 required for the front of particles starting at moment $t = 0$ from the flow entry section ($x = 0$) to reach the given point. Now, considering (3.2), Eq. 3.4a becomes

$$\frac{\partial C'}{\partial t} + \frac{\partial C'}{\partial t_0} = -\varepsilon^* C'. \quad (3.5)$$

Equation 3.5 is a linear first-order partial differential equation. Consider an approach to the solution (integration) of such equations with its transformation into a “characteristic” form.

3.1.2 Basic Analytical Solutions

3.1.2.1 General Solution

The search for such solution implies the transformation of the partial differential equation into a system of ordinary differential equation and the determination of independent integrals of this system (Polyanin et al. 2002). Indeed, Eq. 3.5 corresponds to the system of ordinary differential (characteristic) equations, which can be written in the form of the proportion series:

$$\frac{dt}{1} = \frac{dt_0}{1} = -\frac{1}{\varepsilon^*} \frac{dC'}{C'}. \quad (3.6)$$

The two independent integrals corresponding to the system (3.6) can be represented in two forms:

$$t_0 - t = c_1, \quad C' e^{\varepsilon^* t} = c_2, \quad (3.6a)$$

$$t_0 - t = c_1, \quad C' e^{\varepsilon^* t_0} = c_2, \quad (3.6b)$$

where c_1 and c_2 are integration constants. Therefore, the general solution of the Eq. 3.5 can be expressed in term of an arbitrary function of two arguments, analogous to (1.17), in two forms:

$$\Phi(t_0 - t, C' e^{\varepsilon^* t}) = 0, \quad (3.6c)$$

$$\Phi(t_0 - t, C' e^{\varepsilon^* t_0}) = 0. \quad (3.6d)$$

Solving these relationships for the second argument, we obtain the solution in the form

$$C' = e^{-\varepsilon^* t} \psi(t_0 - t), \quad (3.6e)$$

$$C' = e^{-\varepsilon^* t_0} \psi(t_0 - t), \quad (3.6f)$$

where $\psi(u)$ is an arbitrary function.

3.1.2.2 Explicit Solution

The search for it means the solution of a Cauchy problem for Eq. 3.5 with the initial conditions

$$C' = \varphi_1(t_0) \text{ at } t = 0 \text{ (in this case } t < t_0), \quad (3.7)$$

$$C' = \varphi_2(t) \text{ at } t_0 = 0 \text{ (in this case } t \geq t_0). \quad (3.7a)$$

Functions $\varphi_1(t_0)$ and $\varphi_2(t)$ determine the initial and boundary concentration distributions.

We represent condition (3.7) in the parametric form similarly to (1.37):

$$t = 0, \quad t_0 = \zeta, \quad C' = \varphi_1(\zeta). \quad (3.7b)$$

Substitute the initial data (3.7b) into integrals (3.6a) of the characteristic system (3.6). We find the integration constants: $c_1 = \zeta$, $c_2 = \varphi_1(\zeta)$. Substituting these values in formulas (3.6a), we find the solution of Cauchy problem (3.5), (3.7) in the parametric form

$$t_0 - t = \zeta \quad C' e^{\varepsilon^* t} = \varphi_1(\zeta). \quad (3.7c)$$

Eliminating parameter ζ , we obtain the solution of the Cauchy problem (3.5), (3.7) in the explicit form:

$$C' = e^{-\varepsilon^* t} \varphi_1(t_0 - t). \quad (3.7d)$$

In the case of constant (background) concentration in the aquifer $C(t = 0) = C^0$, we have

$$\varphi_1(t_0 - t) = C_R - C^0, \quad (3.7e)$$

and the solution at $t < t_0$ becomes

$$C = C^0 + (C_R - C^0)(1 - e^{-\varepsilon^* t}). \quad (3.7f)$$

The second solution at (at $t \geq t_0$) of Cauchy problem can be found in the similar manner:

$$C' = e^{-\varepsilon^* t_0} \varphi_2(t_0 - t). \quad (3.8)$$

In the case of constant concentration at the input boundary of the aquifer $C(t_0 = 0)[C(x = 0)] = C_0$

$$\varphi_2(t_0 - t) = C_R - C_0$$

and the solution becomes

$$C = C_0 + (C_R - C_0)(1 - e^{-\varepsilon^* t_0}). \quad (3.8a)$$

The same result can be derived from obvious physical considerations, allowing the initial Eq. 3.5 to be split. Thus, at $t < t_0$ the front of the solution (with concentration C_0) entering the aquifer through the boundary $x = 0$ will not reach the point (section) x and hence $\partial C' / \partial t_0 = 0$ ($\partial C' / \partial x = 0$). The integration of the ordinary differential Eq. 3.5

$$\int_{C_R - C_0}^{C_R - C} \frac{dC'}{C'} = -\varepsilon^* \int_0^t dt. \quad (3.9)$$

yields the solution (3.7f), where C^0 is the background, $C(x, t = 0)$. At $t \geq t_0$, when the front of particles migrating from the left boundary reaches the section x , the transport regime becomes stationary and $\partial C' / \partial t = 0$. Within this time interval, we have

$$\int_{C_R - C_0}^{C_R - C} \frac{dC'}{C'} = -\varepsilon^* \int_0^{t_0} dt, \quad (3.9a)$$

so the process can be described by the stationary asymptotics (3.8a).

3.1.2.3 Specific Cases

They illustrate behavior of the concentration function, $C(t)$ (Fig. 3.1b), under different inflow conditions.

- (1) when the contribution of infiltration water to discharge formation is negligible ($\varepsilon = 0$), we have

$$C = \begin{cases} C^0 & \text{at } t < t_0, \\ C_0 & \text{at } t \geq t_0, \end{cases} \quad t_0 = \frac{x\phi}{q_0}; \quad (3.10)$$

- (2) conversely, if the infiltration completely forms groundwater flow in the horizon ($q_0 = 0$), then

$$C = C^0 + (C_R - C^0)(1 - e^{-\varepsilon^* t}) \quad (t \geq 0); \quad (3.11)$$

whence, in particular, it follows that at $\varepsilon^* t > 3$, the process can be described by stationary asymptotics ($C \approx C_R$), suggesting that infiltration water has almost completely displaced the initial groundwater from the aquifer;

- (3) if the water entering the aquifer at the boundary $x = 0$ contains pollutants in background concentrations ($C_0 = C^0$), then

$$C = \begin{cases} C^0 + (C_R - C^0)(1 - e^{-\varepsilon^* t}) & \text{at } t < t_0, \\ C^0 + (C_R - C^0)(1 - e^{-\varepsilon^* t_0}) & \text{at } t \geq t_0; \end{cases} \quad (3.12)$$

- (4) conversely, if these components occur in the infiltrating water in background concentrations ($C_R = C^0$), then

$$C = \begin{cases} C^0 & \text{at } t < t_0, \\ C_0 + (C^0 - C_0)(1 - e^{-\varepsilon^* t_0}) & \text{at } t \geq t_0. \end{cases} \quad (3.13)$$

Note that all relationships for nonsteady mass transfer contain the complex parameter $\varepsilon^* = \varepsilon/m\phi$, which obviously characterizes the rate of water exchange τ_0 in the aquifer, $\tau_0 \sim 1/\varepsilon^*$. Therefore the evaluation of the complex parameter ε^* is of importance in solving some hydrogeological problems involving the assessment of groundwater protection against pollution, in particular, with substantiation of sanitary protection zones around water supply systems.

3.1.3 Correspondence with a Reservoir Model: Transit Time and Transit Time Distribution

Formally, solution (3.11) can be utilized for description of the transport of a conservative tracer applied during infiltration through an idealized subsurface *catchment flow path* as a representative part of a groundwater system with clearly defined boundaries (groundwater reservoir or catchment). Moreover, the formula (3.11), rewritten for the dimensionless concentration function

$$\bar{C} \equiv F(t) = 1 - \exp\left(-\frac{t}{\tau_0}\right), \quad (3.14)$$

is the relative cumulative frequency distribution of transit times, $F(t)$ (Raats 1984; Haitjema 1995), where

$$\tau_0 = \frac{1}{\varepsilon^*} = \frac{m\phi}{\varepsilon} \quad (3.14a)$$

is the ratio of the total volume of water in the groundwater catchment, $V_w = m\phi S_A$, to the total flux of recharge water, $J_w = \varepsilon S_A$ (S_A is the recharge area). The time constant, τ_0 , is defined as the *turn-over time* (Eriksson 1971; Bolin and Rohde 1973; Etcheverry and Perrochet 2000). In the context of the reservoir theory, function

$F(t)$ is the amount of water particles passing through the outlet boundary of the groundwater catchment flow path (or leaving the groundwater reservoir) per unit time that have spent a time less than or equal to t in the subsurface.

According to (1.123), the solutions $\bar{C}$ and $\bar{C}_i$ for the input stepwise and impulse concentration functions (signals), respectively, are related by the equations

$$\frac{\partial \bar{C}}{\partial \bar{t}} = \bar{C}_i = \frac{m\phi}{P_M} C_i, \quad \bar{t} = \frac{t}{\tau_0}, \quad P_M = \frac{M}{S_A}, \quad (3.14b)$$

where P_M is the density of solute precipitation within the drainage area [ML^{-2}], here M is the mass [M], S_A is the area [L^2]. From here, in particular, we have the solution

$$C_i = \frac{P_M}{m\phi} \exp\left(-\frac{t}{\tau_0}\right), \quad (3.14c)$$

which is of interest in itself.

Function $\bar{C}_i(t)$ is related to the density distribution of transit time. Thus, following the reservoir theory (Eriksson 1971; Raats 1978; Maloszewski and Zuber 1982; Etcheverry and Perrochet 2000; Cornaton and Perrochet 2006), the *mean transit time distribution* (TTD), $g(t)$, can be represented as the response to an instantaneous unit flux impulse over the entire catchment area

$$g(t) = \frac{dF(t)}{dt} = \frac{1}{\tau_0} \exp\left(-\frac{t}{\tau_0}\right) = \frac{1}{\tau_0} \bar{C}_i. \quad (3.14d)$$

The *mean transit time* of a conservative tracer for the catchment flow path is the first normalized moment of the average arrival time of $C_i(t)$ at the catchment outlet (1.129):

$$\tau_m = \frac{m_1}{m_0} = \frac{\int_0^\infty t C_i(t) dt}{\int_0^\infty C_i(t) dt} = \frac{\int_0^\infty t g(t) dt}{\int_0^\infty g(t) dt} \equiv \tau_0, \quad (3.14e)$$

i.e., the mean transit time of particles leaving the catchment is identical with the turn-over time (3.14a). In the general case, the transit time and turn-over time are not necessarily identical (Eriksson 1971). In the context of the reservoir theory, the mean transit time can be associated with the mean age of particles leaving the reservoir (groundwater catchment outlet) (Eriksson 1971; Solomon et al. 2006).

As was mentioned, $g(t)$ conceptually represents the response of the catchment to a unit tracer input. Because of the exponential term in Eq. 3.14d, which accounts for TTD, this model is known as the *exponential model* (Bolin and Rohde 1973; Maloszewski and Zuber 1982; Solomon et al. 2006). Actually, there exist different types of TTDs used for description of hydrological systems. Along with the exponential model, common model types include (Maloszewski and Zuber 1982; McGuire and McDonnell 2006; Cornaton and Perrochet 2006): piston flow, combined exponential-piston mixing, and dispersive mixing.

In the case of time-variable concentration in the recharged water, the transport of conservative tracer through a catchment flow path can be described by a *convolution*

integral (Gelhar and Wilson 1974; Raats 1978, 1984; Duffy and Gelhar 1985; Zoellmann et al. 2001; Kirchner et al. 2000; McGuire and McDonnell 2006), implying that the outflow concentration, $C(t)$, results from mixing of tracer solutions with concentrations $C_R(t - \tau)$ that fell uniformly on the catchment in the moment $(t - \tau)$ in the past and reached the outlet with a lag described by the transit time distribution, $g(t)$:

$$C(t) = \int_0^{\infty} g(\tau) C_R(t - \tau) d\tau = g(t) * C_R(t), \quad (3.14f)$$

where $g(t)$ has a meaning of *transfer function*, τ is the lag time between tracer input and output (Eriksson 1961; Raats 1978; McGuire and McDonnell 2006); the asterisk is the denotation of the convolution operation.

Thus, with the tracer concentration in infiltration water linearly increasing over time

$$C_R(t) = C^0 + G_R t$$

the solution of the problem becomes

$$C(t) = C^0 + G_R \left[(t - \tau_0) + \tau_0 \exp\left(-\frac{t}{\tau_0}\right) \right], \quad (3.14g)$$

whence it follows that for a long-lasting migration process ($t \gg \tau_0$), the output concentration function is also linear, though its plot $C(t)$ is the function $C_R(t)$ shifted by τ_0 to the right along the time axis; here G_R is the time gradient of concentration [$\text{ML}^{-3}\text{T}^{-1}$].

If $C_R(t)$ is considered as a function reflecting a stationary stochastic process, the solution for the output concentration function $C(t)$ can also be found in terms of a stochastic model (Duffy and Gelhar 1985). In this case, the sensitivity of the linear model to variations in the input concentration can be examined. Such analysis shows the ratios of statistical dispersions of the output (σ_C^2) to input ($\sigma_{C_R}^2$) concentration functions to be

$$\frac{\sigma_C^2}{\sigma_{C_R}^2} = \frac{1}{1 + \tau_0/\lambda}, \quad (3.14h)$$

where λ is the correlation time scale for function $C_R(t)$ [T].

From here it follows that variations in the atmospheric water chemistry in the discharge zone of groundwater flow can be reliably evaluated only when the values of time characteristics τ_0 and λ are comparable. Otherwise, e.g., when $\tau_0 \gg \lambda$, the dispersion σ_C^2 is close to zero, meaning that variations in infiltration water chemistry are almost impossible to assess based on groundwater sampling data. Such estimates are of use in the analysis and planning of groundwater isotopic monitoring. Thus, it can be easily shown that seasonal variations in the isotopic composition of atmospheric precipitation ($\lambda = 1/2 - 1/4$ yr) cannot be reliably determined in hydrogeological systems with characteristic water exchange time of tens of years and more ($\tau_0 > n10$ yrs).

As shown below (Sect. 4.2.2, Formula 4.11), the averaging of concentration over the section for flow model in a two-dimensional vertical plane in a semirestricted bed (see Fig. 4.1a) also yields the ideal mixing model (3.14), (3.14c). From the physical point of view, $\bar{C}$ and $\bar{C}_i$ are path-integrated concentrations that represent all possible flow pathways in the cross-section and show a mixture of ages, which may range between several orders of magnitude. Therefore the functions $F(t)$ and $g(t)$ presented above effectively integrate different residence (transit) times. As one may see, these functions are insensitive to the horizontal scale (catchment size and shape) and independent of regional variations in the hydraulic conductivity (Haitjema 1995).

To determine the mean residence time, τ_m , in practice one can choose among a series of techniques based on environmental tracers (Sects. 3.4.1, 3.4.2 and 4.2.3). The independence of τ_m (3.14e) on the horizontal scale is a fundamental attribute of an aquifer that receives uniform recharge and has a constant thickness (Solomon et al. 2006). Having collected flow integrated samples of discharge anywhere in the catchment, one may, in theory, evaluate the most important properties of a subsurface hydrological system associated with groundwater recharge (ϵ) and static storage ($m\phi$). These findings are also of significance for assessing groundwater vulnerability.

3.2 Transport of a Solute Subject to First-Order Single-Stage Decay

3.2.1 Basic Analytical Solutions

If the decay is described by the first-order kinetic equation (1.197), the function W_s in the balance Eq. 1.12 can be represented in the following generalized form:

$$W_s = W_s^\lambda + W_s^\epsilon = \phi\lambda C - \frac{\epsilon}{m}C_R; \quad (3.15)$$

here λ is decay constant [T^{-1}].

Transformations of Eq. 1.12 similar to those described above (considering the first equality 3.3) yield for the one-dimensional case

$$\frac{\partial C}{\partial t} + \frac{\partial C}{\partial t_0} + (\epsilon^* + \lambda)C - \epsilon^*C_R = 0. \quad (3.16)$$

With the identification of two characteristic migration regimes (see Sect. 3.1.2.2), Eq. 3.16 can be replaced by the two ordinary differential equations

$$\begin{aligned} \frac{dC}{dt} + (\epsilon^* + \lambda)C &= \epsilon^*C_R \quad \text{at } t < t_0, \\ \frac{dC}{dt_0} + (\epsilon^* + \lambda)C &= \epsilon^*C_R \quad \text{at } t \geq t_0. \end{aligned} \quad (3.17)$$

We solve Eqs. 3.17 by the operation method. Thus a generalized representation of (3.17) in Laplace transforms (1.94) with a nonzero initial condition (Doetsch 1967) has the form

$$p\tilde{C} - C^0(C_0) + (\varepsilon^* + \lambda)\tilde{C} = \frac{\varepsilon^* C_R}{p}, \quad (3.18)$$

whence we have

$$\tilde{C} = \frac{\varepsilon^* C_R}{p(p + \varepsilon^* + \lambda)} + \frac{C^0(C_0)}{p + \varepsilon^* + \lambda}; \quad (3.19)$$

here C^0 and $\tilde{C} \equiv \tilde{C}(t)$ at $t < t_0$; C_0 and $\tilde{C} \equiv \tilde{C}(t_0)$ at $t \geq t_0$.

The inverse transform of function $\tilde{C}$ can be obtained using standard tables (Bateman and Erdelyi 1954). The final solution of Eq. 3.16 has the generalized form

$$\bar{C} = \frac{C - C^0(C_0)}{C_R - C^0(C_0)} = F(t, t_0), \quad (3.20)$$

where

$$F(t, t_0) = \begin{cases} F(t) = \frac{1}{1 + \lambda_\varepsilon} (1 - e^{-\varepsilon^*(1 + \lambda_\varepsilon)t}) & \text{at } t < t_0, \\ F(t_0) = \frac{1}{1 + \lambda_\varepsilon} (1 - e^{-\varepsilon^*(1 + \lambda_\varepsilon)t_0}) & \text{at } t \geq t_0, \end{cases} \quad (3.21)$$

$$\lambda_\varepsilon = \lambda/\varepsilon^* = \lambda m\phi/\varepsilon.$$

Considering the logarithmic character of function t_0 (3.2), the steady phase of the process (at $t \geq t_0$) can be shown to have the spatial distribution $C(x)$

$$\frac{C - C_0}{C_R - C_0} = \frac{1}{1 + \lambda_\varepsilon} \left[1 - \left(1 + \frac{\varepsilon^*}{u_0} x \right)^{-(1 + \lambda_\varepsilon)} \right]. \quad (3.22)$$

3.2.2 Variable Boundary Conditions

3.2.2.1 The Case of $C_R = f(t)$

The description of a migration process often requires the resulting solution to reflect time variations in solute concentration in infiltration water: $C_R = C_R(t)$. If function $C_R(t)$ admits piecewise-homogeneous (step-wise) representation, such that $C_R^i = C_R^{i-1} + \Delta C_R^{i-1}$ (ΔC_R^{i-1} is the increment of the boundary concentration at moment t^{i-1} ; $i = 1, 2, \dots$ are the numbers of time intervals within which it is assumed that $C_R = C_R^i = \text{const}$), the corresponding relationships can be obtained by the superposition of the above basic solution for function $F(t, t_0)$:

$$C^i = C^0 + \sum_{j=1}^i (C_R^j - C_R^{j-1}) F(t^i - t^{j-1}) \text{ at } t^{j-1} < t^i < t_0^i, \quad (3.23a)$$

where $C_R^0 = C^0$, $t_0^0 = 0$;

$$C^i = C_0 + \sum_{j=1}^i (C_R^j - C_R^{j-1}) F(t_0^i - t_0^{j-1}) \text{ at } t^i \geq t_0^i, \quad (3.23b)$$

where $C_R^0 = C_0$, $t_0^0 = 0$.

For the continuous analytical function $C_R = C_R(t)$, the mathematical model is the convolution integral (Solomon et al. 2006)

$$C(t) = \int_0^\infty g(\tau) C_R(t - \tau) e^{-\lambda \tau} d\tau; \quad (3.24)$$

all functions are determined as in (3.14f).

3.2.2.2 The Case of $C_R = f(x)$, $\varepsilon = f(x)$

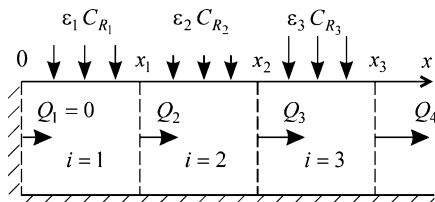
To construct the relationships taking into account the spatial variations in the concentration function and the rate of groundwater infiltration recharge, one can use partial solutions of migration problems with piecewise-homogeneous representation of functions $\varepsilon(x)$ and $C(x)$, as shown in Fig. 3.2.

Consider, for example, a model of a three-zone flow, in which sections x_1 , x_2 and x_3 are boundaries between zones differing by the values of functions C_{R_i} and ε_i ($i = 1, 2, 3$). The groundwater flow discharges Q_i at the boundaries between zones can be readily calculated from liquid balance equations.

The migration process within the identified zones (1, 2 and 3) can be described by the following equations:

$$\begin{aligned} m\phi \frac{\partial C_1}{\partial t} + \frac{\partial}{\partial x} [(Q_1 + \varepsilon_1 x) C_1] + \lambda m\phi &= \varepsilon_1 C_{R_1}, \\ m\phi \frac{\partial C_2}{\partial t} + \frac{\partial}{\partial x} [(Q_2 + \varepsilon_2 x) C_2] + \lambda m\phi &= \varepsilon_2 C_{R_2}, \\ m\phi \frac{\partial C_3}{\partial t} + \frac{\partial}{\partial x} [(Q_3 + \varepsilon_3 x) C_3] + \lambda m\phi &= \varepsilon_3 C_{R_3}. \end{aligned} \quad (3.25)$$

Fig. 3.2 Conceptual diagram showing piecewise distribution of the input functions, ε and C_R (three-zone model)



The introduction of a new coordinate system (t, t_{0i}) allows (3.25) to be represented in the following generalized form:

$$\frac{\partial C_i}{\partial t} + \frac{\partial C_i}{\partial t_{0i}} + \epsilon_i^* (1 + \lambda_{\epsilon i}) C_i = \epsilon_i^* C_{Ri}, \quad i = 1, 2, 3; \quad (3.26)$$

here the derivative $\partial C_i / \partial t_{0i}$ accounts for variations in solute concentration within the i th zone at the front that started its motion from the interface between the $i - 1$ and i zones in the moment $t = 0$; $\epsilon_i^* = \epsilon_{Ri} / m\phi$, $\lambda_{\epsilon i} = \lambda / \epsilon_i^*$.

Thus, the solutions describing variations in solute concentration in points x_1 , x_2 and x_3 , will be further related to the particle residence times within the identified zones:

$$t_{0i} = \frac{1}{\epsilon_i^*} \ln \left(1 + \frac{\epsilon_i^* (x_i - x_{i-1})}{\sum_{j=2}^i \epsilon_{i-1}^* (x_{i-1} - x_{i-2})} \right), \quad i = 2, 3; \quad (3.27)$$

such that $t = t_{02}$ and $t = t_{02} + t_{03}$ are particle migration times between sections x_1 and x_2 , and x_1 and x_3 , respectively.

Thus the generalized solution of (3.26) for points x_1 at $t > 0$, x_2 at $0 < t < t_{02}$, and x_3 at $0 < t < t_{03}$ in the accepted notations becomes (see Sect. 3.2.1, zero initial condition)

$$C_i = \frac{C_{Ri}}{1 + \lambda_{\epsilon i}} (1 - e^{-\alpha_i t}), \quad (3.28)$$

where $\alpha_i = \epsilon_i^* (1 + \lambda_{\epsilon i})$.

Since the flux at the left boundary of the 1st zone $Q_1 = 0$, Eq. 3.28 provides a full solution of the problem for the section $x = x_1$. Clearly this solution should be regarded as the boundary condition for solving the Eq. 3.26 ($i = 2$), describing variations in concentration $C = C_2$ in point x_2 for time $t > t_{02}$:

$$C_2(t_{02} = 0, t) = C_1(t) = \frac{C_{R1}}{1 + \lambda_{\epsilon_1}} (1 - e^{-\alpha_1 t}). \quad (3.29)$$

With passage to Laplace transforms, the Eq. 3.26 ($i = 2$) becomes the ordinary differential equation

$$\frac{d\tilde{C}_2}{dt_{02}} + (p + \alpha_2)\tilde{C}_2 = \frac{\alpha_2}{(1 + \lambda_{\epsilon_2})p} C_{R2}. \quad (3.30)$$

Its general solution can be found by substituting $\tilde{C}_2 = uv$, whence

$$\tilde{C}_2 = \frac{\alpha_2}{(1 + \lambda_{\epsilon_2})(p + \alpha_2)p} C_{R2} + ce^{-(p + \alpha_2)t_{02}}. \quad (3.31)$$

The integration constant c can be found from the condition $t_{02} = 0 \quad \tilde{C}_2 = \tilde{C}_1$, which in terms of transforms becomes

$$\tilde{C}_1 = \frac{C_{R_1}}{(1 + \lambda_{\epsilon_1})p} + \frac{C_{R_1}}{(1 + \lambda_{\epsilon_1})(p + \alpha_1)}. \quad (3.32)$$

Finally we obtain:

$$\begin{aligned} \tilde{C}_2 = & \frac{\alpha_2 C_{R_2}}{(1 + \lambda_{\epsilon_2})(p + \alpha_2)p} (1 - e^{-(p + \alpha_2)t_{02}}) + \frac{C_{R_1}}{(1 + \lambda_{\epsilon_1})p} e^{-(p + \alpha_2)t_{02}} \\ & - \frac{C_{R_1}}{(1 + \lambda_{\epsilon_1})(p + \alpha_1)} e^{-(p + \alpha_2)t_{02}}. \end{aligned} \quad (3.33)$$

Tables (Bateman and Erdelyi 1954) are used to invert the latter formula. The required solution has the form

$$C_2 = \frac{C_{R_2}}{1 + \lambda_{\epsilon_2}} (1 - e^{-\alpha_2 t_{02}}) + \frac{C_{R_1}}{1 + \lambda_{\epsilon_1}} e^{-\alpha_2 t_{02}} (1 - e^{-\alpha_1(t - t_{02})}). \quad (3.34)$$

Similarly, the solutions can be found for the function C_3 in the ranges $t_{03} < t < (t_{03} + t_{02})$, when the boundary condition for equation (3.26, $i = 3$) is represented by the condition (3.28, $i = 2$), and $t > (t_{03} + t_{02})$, when the function $C_3(t_{03} = 0, t) = C_2$ (3.34). As the result we have:

$$C_3 = \frac{C_{R_3}}{1 + \lambda_{\epsilon_3}} (1 - e^{-\alpha_3 t_{03}}) + \frac{C_{R_2}}{1 + \lambda_{\epsilon_2}} e^{-\alpha_3 t_{03}} (1 - e^{-\alpha_2(t - t_{03})}) \quad (3.35)$$

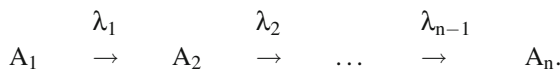
– at $t_{03} < t < (t_{03} + t_{02})$;

$$\begin{aligned} C_3 = & \frac{C_{R_3}}{1 + \lambda_{\epsilon_3}} (1 - e^{-\alpha_3 t_{03}}) + \frac{C_{R_2}}{1 + \lambda_{\epsilon_2}} e^{-\alpha_3 t_{03}} (1 - e^{-\alpha_2 t_{02}}) \\ & + \frac{C_{R_1}}{1 + \lambda_{\epsilon_1}} e^{-\alpha_2 t_{02}} e^{-\alpha_3 t_{03}} (1 - e^{-\alpha_1(t - t_{02} - t_{03})}) \end{aligned} \quad (3.36)$$

– at $t > (t_{03} + t_{02})$.

3.3 Migration of a Solute Subject to Chain Decay

The decay of a migrating component, e.g., an unstable (radioactive) isotope, can result in the formation of unstable components (isotopes), which can farther decay:



The migration models that consider the entire chain of chemical or nuclear transformations are of interest when the newly formed components are a hazard or

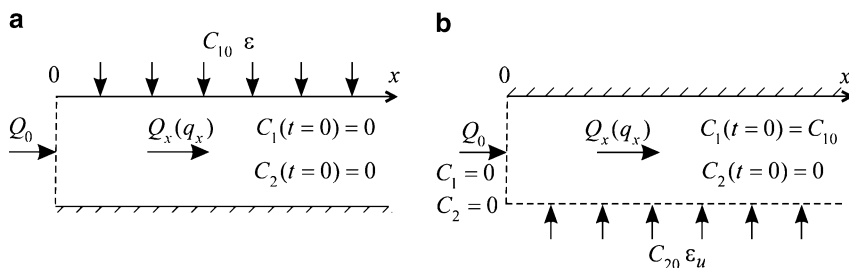


Fig. 3.3 Conceptual schemes for deriving relationships describing isotopic dating of groundwater: (a) in the case of input of an unstable isotope into the aquifer through infiltration; (b) in the case of decay of a radioactive element contained in water-bearing rocks

when studying the coexistence in the solution of the parent matter and the daughter products of their decay facilitates groundwater dating (based on isotopic data). In this context we consider the construction of relationships describing the formation conditions of groundwater isotopic composition in two typical situations:

- (1) an unstable (radioactive) component enters an aquifer with infiltration water, where it decays, releasing a daughter isotope (Fig. 3.3a);
- (2) the source of radioactivity is the rock itself, and the decay of elements it contains results in the accumulation of fission products in groundwater (Fig. 3.3b).

3.3.1 Two-Stage Chain Decay of an Unstable Isotope Coming into an Aquifer with Infiltration Recharge

3.3.1.1 General Solution

The governing system of equations comprises the mass balance equations of the parent (A_1) and daughter (A_2) components:

$$\begin{aligned} \phi \frac{\partial C_1}{\partial t} + \frac{\partial}{\partial x}(q_x C_1) + \lambda_1 \phi C_1 - \frac{\varepsilon}{m} C_{10} &= 0, \\ \phi \frac{\partial C_2}{\partial t} + \frac{\partial}{\partial x}(q_x C_2) + \lambda_2 \phi C_2 - \lambda_1 \phi C_1 &= 0; \end{aligned} \quad (3.37)$$

here C_1 and C_2 are concentrations of isotopes A_1 and A_2 ; C_{10} is the concentration of isotope A_1 in the infiltrating water; by concentration C_i we mean the number of atoms A_i able to decay per unit volume [L^{-3}]; the volumetric activity

$$[A_i] = \lambda_i C_i [L^{-3} T^{-1}].$$

The boundary and initial conditions:

$$C_1(x=0) = 0, \quad C_2(x=0) = 0, \quad C_1(t=0) = 0, \quad C_2(t=0) = 0. \quad (3.38)$$

The substitution of q_x (3.1a) into the system of Eqs. 3.37 yields

$$\begin{aligned}\frac{\partial C_1}{\partial t} + \frac{\partial C_1}{\partial t_0} + (\lambda_1 + \varepsilon^*)C_1 &= \varepsilon^*C_{10}, \\ \frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial t_0} + (\lambda_2 + \varepsilon^*)C_2 &= \lambda_1 C_1.\end{aligned}\quad (3.39)$$

With the zero boundary conditions (3.38), the first equation in (3.39) has a solution similar to (3.20) with the substitution $C = C_1$ and $\lambda = \lambda_1$:

$$C_1 = C_{10} \frac{\varepsilon^*}{\lambda_1 + \varepsilon^*} (1 - e^{-(\lambda_1 + \varepsilon^*)t'}), \quad (3.40)$$

where $t' = t (< t_0)$ for the transient phase of the process and $t' = t_0 (< t)$ for the steady-state phase of the process.

Now the second equation in (3.39) for C_2 can be transformed into the generalized form

$$\frac{dC_2}{dt'} + (\lambda_2 + \varepsilon^*)C_2 = \frac{\lambda_1 \varepsilon^* C_{10}}{\lambda_1 + \varepsilon^*} (1 - e^{-(\lambda_1 + \varepsilon^*)t'}). \quad (3.41)$$

The solution of the ordinary differential Eq. 3.41 has the form

$$C_2 = \frac{\lambda_1 \varepsilon^* C_{10}}{(\lambda_1 + \varepsilon^*)(\lambda_2 + \varepsilon^*)} \left[\frac{\lambda_2 + \varepsilon^*}{\lambda_1 - \lambda_2} e^{-(\lambda_1 + \varepsilon^*)t'} - \frac{\lambda_1 + \varepsilon^*}{\lambda_1 - \lambda_2} e^{-(\lambda_2 + \varepsilon^*)t'} + 1 \right]. \quad (3.42)$$

The formal analysis of solutions (3.40) and (3.42) suggests the conclusion that the concentration ratio of the daughter to parent isotope, $\bar{C}_{21}$, does not depend on radioactive isotope concentration, C_{10} , in the infiltration water:

$$\begin{aligned}\bar{C}_{21} = \frac{C_2}{C_1} &= \frac{\lambda_1}{(\lambda_2 + \varepsilon^*)} (1 - e^{-(\lambda_1 + \varepsilon^*)t'})^{-1} \\ &\times \left[\frac{\lambda_2 + \varepsilon^*}{\lambda_1 - \lambda_2} e^{-(\lambda_1 + \varepsilon^*)t'} - \frac{\lambda_1 + \varepsilon^*}{\lambda_1 - \lambda_2} e^{-(\lambda_2 + \varepsilon^*)t'} + 1 \right].\end{aligned}\quad (3.43)$$

Let us analyze the behavior of function $\bar{C}_{21}$ at fixed λ_1 and λ_2 .

In the time interval $t < t_0$, i.e., while water that enters the aquifer through the inlet boundary $x = 0$ has not reached the point x , the function $\bar{C}_{21}$ steadily increases with a rate determined by the complex parameter ε^* . This period can last indefinitely if the aquifer is separated by a water divide line (since $Q_0 = 0$, $t_0 \rightarrow \infty$). If it is known a priori that $t > (3 \div 5)/(\lambda_{1,2} + \varepsilon^*)$, we have

$$\bar{C}_{21} = \frac{\lambda_1}{(\lambda_2 + \varepsilon^*)}, \quad (3.44)$$

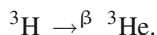
i.e., given the concentration ratio of the two isotopes $\bar{C}_{21}$, we can calculate the parameter ε^* , which characterizes the rate of water exchange in the aquifer.

The effect of the recharge boundary at $t \geq t_0$ manifests itself in the stabilization of $\bar{C}_{21}$; the steady-state estimated values of $\bar{C}_{21}$ depend on t_0 (i.e., on the position of the point relative to the inlet boundary (x coordinate)), water discharge Q_0 , and parameter ϵ^* (see Formula 3.2).

Clearly, the interpretation of isotopic data is more reliable in closed groundwater basins receiving exclusively infiltration recharge. Now, in the general case, given information about the moment when the first portions of atmospheric water, containing a radioactive isotope, entered the aquifer, one can use the solution (3.44) to gain an impression about the value of the complex parameter ϵ^* .

3.3.1.2 Special Case: Tritium-Helium-3 Method of Groundwater Dating

Of particular interest in the context of groundwater dating based on isotopic data is the case with $\lambda_2 = 0$, corresponding to the decay of a radioactive isotope with the formation of a stable daughter isotope. This is the case, for example, when water entering the aquifer is high in tritium (^3H), whose β -decay product is helium isotope (^3He)



The decay constant $\lambda_1 = \ln 2/T_{1/2} = 0.0565 \text{ yr}^{-1}$; $T_{1/2} = 12.264$ yrs is the half-life period (Akulov and Mamyryn 2004).

The method of experimental studying of those isotopes for groundwater dating was called *tritium-helium-3* ($^3\text{H}/^3\text{He}$) *method*. Tolstikhin and Kamensky (1969) are believed to pioneer in this field. The method has been widely used in hydrogeology, in particular, in studying groundwater infiltration recharge (Solomon and Sudicky 1991; Solomon et al. 1993; Mook 2000), as well as in verifying mathematical (numerical) models of hydrogeological systems (Mattle et al. 2001).

In the cases where a stable decay product is used (^3He , in this case), the expressions (3.40), (3.42) and (3.43) can be represented in the dimensionless form:

$$\bar{C}_1 = \frac{\bar{\epsilon}}{1 + \bar{\epsilon}} (1 - e^{-(1+\bar{\epsilon})\bar{t}}), \quad (3.45)$$

$$\bar{C}_2 = \frac{1}{(1 + \bar{\epsilon})} [\bar{\epsilon} e^{-(1+\bar{\epsilon})\bar{t}} - (1 + \bar{\epsilon}) e^{-\bar{\epsilon}\bar{t}} + 1], \quad (3.46)$$

$$\bar{C}_{21} = \frac{1}{\bar{\epsilon}} (1 - e^{-(1+\bar{\epsilon})\bar{t}})^{-1} [\bar{\epsilon} e^{-(1+\bar{\epsilon})\bar{t}} - (1 + \bar{\epsilon}) e^{-\bar{\epsilon}\bar{t}} + 1], \quad (3.47)$$

where $\bar{C}_1 = C_1/C_{10}$, $\bar{C}_2 = C_2/C_{10}$, $\bar{C}_{21} = \bar{C}_2/\bar{C}_1$, $\bar{\epsilon} = \epsilon^*/\lambda_1$ and $\bar{t} = \lambda_1 t < \lambda_1 t_0$ (see also plots of functions $\bar{C}_1$, $\bar{C}_2$ and $\bar{C}_{21}$ in Fig. 3.4).

It can be easily seen that the concentration $\bar{C}_2$ can be calculated as the difference between the solution of appropriate problem obtained for $\bar{C}_1$ (3.7e) in the absence of radioactive decay minus the solution $\bar{C}_1$ (3.21) for the one-stage decay, i.e.,

$$\bar{C}_2 = \bar{C}_1|_{\lambda_1=0} - \bar{C}_1|_{\lambda_1>0}. \quad (3.48)$$

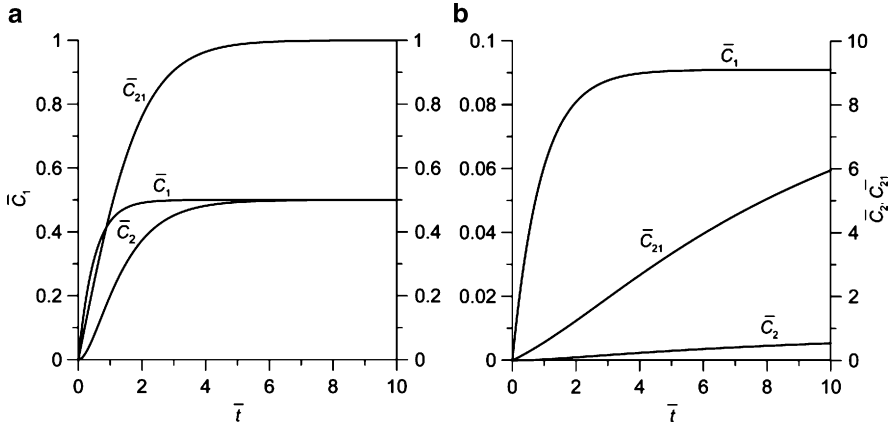


Fig. 3.4 Plots of functions $\bar{C}_1 = C_1/C_{10}$, $\bar{C}_2 = C_2/C_{10}$ and $\bar{C}_{21} = C_2/C_1$ at different $\bar{\varepsilon} = \varepsilon/m\phi\lambda_1$. (a) $\bar{\varepsilon} = 1.0$, (b) $\bar{\varepsilon} = 0.1$

This approach to evaluating the concentration $\bar{C}_2$ (and hence, $\bar{C}_{21}$ as well) can be effectively used in numerical modeling of groundwater isotopic composition (Mattle et al. 2001).

In practical calculations, the atomic concentrations C_1 and C_2 are commonly converted into volumetric concentrations (Sect. 3.3.5).

3.3.2 Two-Stage Chain Decay in Aquifer with a Radioactive Element in Solids as the Only Source of Radioactivity

Suppose that the radioactivity source for groundwater is the porous rock matrix (Fig. 3.3b). The initial (at $t = 0$) radionuclide concentration in it is C_{10} . The specific discharge of groundwater flow at the inlet boundary of the aquifer ($x = 0$) is assumed to be constant (Q_0). This flow supplies to the aquifer only clear water containing neither parent (A_1), nor daughter (A_2) isotope: $C_1(x = 0) = 0$, $C_2(x = 0) = 0$. Additionally, the model allows for the leakage of deeper water with a specific rate of ε_u . This water carries A_2 in concentration C_{20} , such that its mass flux is $J_0 = \varepsilon_u C_{20}$. The major difficulties with the correct interpretation of isotopic monitoring data are often associated with evaluating this characteristic of the regional flux J_0 (see Sect. 3.4.4).

The system of equations of isotopic balance has the form:

$$\begin{aligned} \frac{\partial C_1}{\partial t} + \lambda_1 C_1 &= 0, \\ \phi \frac{\partial C_2}{\partial t} + \frac{\partial}{\partial x}(q_x C_2) + \lambda_2 \phi C_2 - \lambda_1 k_1 C_1 - \frac{\varepsilon_u}{m} C_{20} &= 0, \end{aligned} \quad (3.49)$$

where C_1 is the number of atoms able to decay in a unit rock volume; C_2 is the number of atoms able to decay in a unit volume of pore solution (groundwater); k_1 is the number of daughter atoms resulting from the decay of a single atom of the parent element; $q_x = \varepsilon_u x/m + Q_0/m$. Considering the latter relationship, the system of Eqs. 3.49 becomes

$$\begin{aligned} \frac{\partial C_1}{\partial t} + \lambda_1 C_1 &= 0, \\ \frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial t_0} + (\varepsilon^* + \lambda_2) C_2 - \lambda_1 \frac{k_1}{\phi} C_1 &= \varepsilon^* C_{20}, \end{aligned} \quad (3.50)$$

where $\varepsilon^* = \varepsilon_u/m\phi$.

By using Laplace transform and considering the initial condition $C_1(t=0) = C_{10}$, we obtain an analogue of the system of Eqs. 3.50 in images:

$$\begin{aligned} (p + \lambda_1) \tilde{C}_1 &= C_{10}, \\ \frac{d\tilde{C}_2}{dt_0} + (p + \varepsilon^* + \lambda_2) \tilde{C}_2 &= \frac{k_1}{\phi} \frac{\lambda_1 C_{10}}{p + \lambda_1} + \frac{\varepsilon^* C_{20}}{p}. \end{aligned} \quad (3.51)$$

The former equation belongs to the class of algebraic equations and has a trivial solution. The second equation in (3.51) is a first-order differential equation. Its solution can be found with the substitution $\tilde{C}_2 = uv$. We obtain:

$$\tilde{C}_1 = \frac{C_{10}}{p + \lambda_1}; \quad (3.52)$$

$$\begin{aligned} \tilde{C}_2 &= \frac{k_1}{\phi} \frac{\lambda_1 C_{10}}{(p + \lambda_1)(p + \varepsilon^* + \lambda_2)} + \frac{\varepsilon^* C_{20}}{p(p + \varepsilon^* + \lambda_2)} \\ &+ \left(\frac{k_1}{\phi} \frac{\lambda_1 C_{10}}{(p + \lambda_1)(p + \varepsilon^* + \lambda_2)} + \frac{\varepsilon^* C_{20}}{p(p + \varepsilon^* + \lambda_2)} \right) e^{-(p + \varepsilon^* + \lambda_2)t_0}. \end{aligned} \quad (3.53)$$

The inversion of functions $\tilde{C}_1$ and $\tilde{C}_2$ yields the originals:

$$C_1 = C_{10} e^{-\lambda_1 t}; \quad (3.54)$$

$$C_2 = \frac{k_1}{\phi} \frac{\lambda_1 C_{10}}{(\lambda_1 - \lambda_2 - \varepsilon^*)} (e^{-(\lambda_2 + \varepsilon^*)t} - e^{-\lambda_1 t}) + \frac{\varepsilon^* C_{20}}{\varepsilon^* + \lambda_2} (1 - e^{-(\lambda_2 + \varepsilon^*)t}) \quad (3.55)$$

– at $t < t_0$,

$$C_2 = \frac{k_1}{\phi} \frac{\lambda_1 C_{10}}{(\lambda_1 - \lambda_2 - \varepsilon^*)} (e^{-(\lambda_2 + \varepsilon^*)t_0} e^{-\lambda_1(t-t_0)} - e^{-\lambda_1 t}) + \frac{\varepsilon^* C_{20}}{\varepsilon^* + \lambda_2} (1 - e^{-(\lambda_2 + \varepsilon^*)t_0}) \quad (3.55a)$$

– at $t \geq t_0$.

If the decay of the daughter product can be neglected, i.e., $\lambda_2 = 0$, the Eqs. 3.54–3.55 become simpler and can be written as

$$C_1 = C_{10}e^{-\bar{t}}, \quad (3.56)$$

$$C_2 = \frac{k_1}{\phi} \frac{C_{10}e^{-\bar{t}}}{(1-\bar{\epsilon}_\lambda)} (e^{(1-\bar{\epsilon}_\lambda)\bar{t}} - 1) + C_{20}(1 - e^{-\bar{\epsilon}_\lambda\bar{t}}) \quad (3.57)$$

– at $t < t_0$,

$$C_2 = \frac{k_1}{\phi} \frac{C_{10}e^{-\bar{t}}}{(1-\bar{\epsilon}_\lambda)} (e^{(1-\bar{\epsilon}_\lambda)\bar{t}_0} - 1) + C_{20}(1 - e^{-\bar{\epsilon}_\lambda\bar{t}_0}) \quad (3.57a)$$

– at $t \geq t_0$;

here $\bar{\epsilon}_\lambda = \epsilon^*/\lambda_1$, $\bar{t} = \lambda_1 t$, $\bar{t}_0 = \lambda_1 t_0$.

If we assign $\epsilon_u = 0$, i.e., neglect the regional (“background”) flux of natural isotopes of the daughter decay product through the aquifer floor, the Eqs. 3.57 and 3.57a can be presented in the dimensionless form

$$\bar{C}_2^{\phi k} = \frac{\phi}{k_1} \frac{C_2}{C_{10}} = (1 - e^{-\lambda_1 t}) \text{ at } t < t_0, \quad (3.58)$$

$$\bar{C}_2^{\phi k} = \frac{\phi}{k_1} \frac{C_2}{C_{10}} = (e^{-\lambda_1(t-t_0)} - e^{-\lambda_1 t}) \text{ at } t \geq t_0. \quad (3.58a)$$

The substitution of C_{10} from formula (3.56) into (3.57) and (3.57a) yields:

$$\bar{C}_{21}^{\phi k} = \frac{\phi}{k_1} \frac{C_2}{C_1} = (e^{\lambda_1 t} - 1) \text{ at } t < t_0, \quad (3.59)$$

$$\bar{C}_{21}^{\phi k} = \frac{\phi}{k_1} \frac{C_2}{C_1} = (e^{\lambda_1 t_0} - 1) \text{ at } t \geq t_0. \quad (3.59a)$$

Since $\epsilon_u = 0$, we have $t_0 = xm\phi/Q_0 = \phi x/q_0$. Plots of solutions (3.56) and (3.59) are given in Fig. 3.5.

3.3.3 Two-Member Chain Decay in Aquifer Solids Containing Several Radioactive Elements

Now suppose that the radioactivity of the aquifer solids is due to the presence of several ($j = 1, 2, \dots, J$) elements able to decay, and the decay of each atom of the j th isotope results in the formation of k_j daughter atoms. The initial atomic concentration of each element is C_{10}^j . In this case, the system of isotopic balance equations becomes

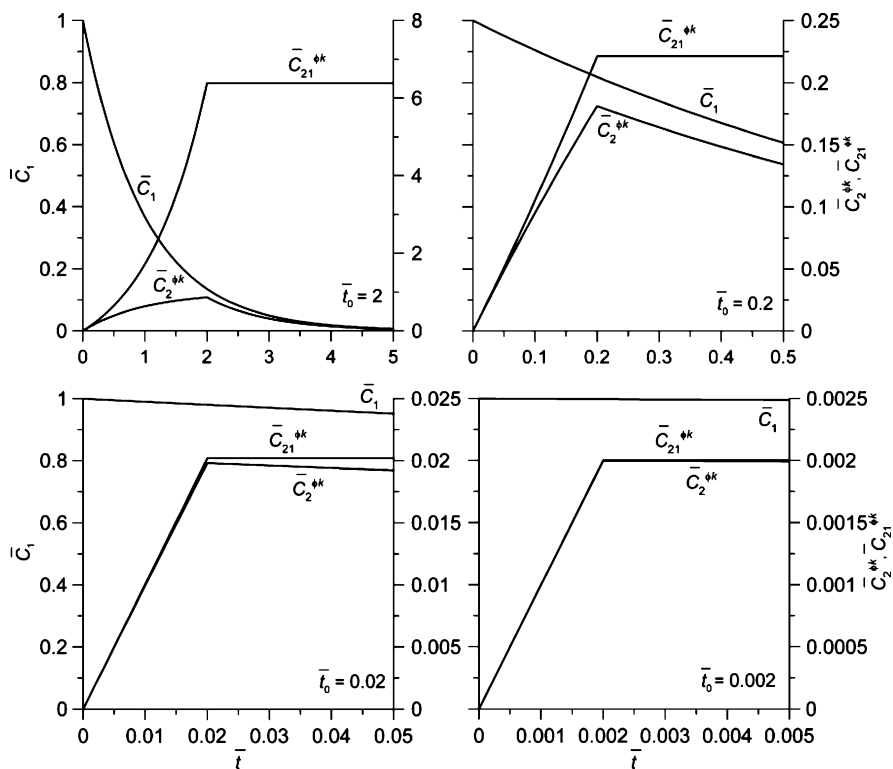


Fig. 3.5 Plots of functions $\bar{C}_1 = C_1/C_{10}$, $\bar{C}_2^{\phi k}$ and $\bar{C}_{21}^{\phi k}$ at different $\bar{t}_0 : 2, 0.2, 0.02, 0.002$ ($\bar{t} = \lambda_1 t$, $\bar{t}_0 = \lambda_1 t_0$)

$$\begin{aligned}
 \frac{\partial C_1^1}{\partial t} + \lambda_1^1 C_1^1 &= 0, \\
 \frac{\partial C_1^2}{\partial t} + \lambda_1^2 C_1^2 &= 0, \\
 &\dots\dots\dots, \\
 \frac{\partial C_1^j}{\partial t} + \lambda_1^j C_1^j &= 0, \\
 \phi \frac{\partial C_2}{\partial t} + \frac{\partial}{\partial x}(q_x C_2) + \lambda_2 \phi C_2 - \sum_{j=1}^{j=J} \lambda_1^j k_j C_1^j - \frac{\epsilon_u}{m} C_{20} &= 0, \quad (3.60)
 \end{aligned}$$

where j is the conventional (ordinal) number of the radioactive element, λ_1^j its decay constant.

This system is linear, therefore its solution presents no mathematical problems. The result is

$$C_1^j = C_{10}^j e^{-\lambda_1^j t}, \quad (3.61)$$

$$C_2 = \frac{1}{\phi} \sum_{j=1}^J \frac{k_j \lambda_1^j C_{10}^j}{(\lambda_1^j - \lambda_2^- \epsilon^*)} e^{-\lambda_1^j t} \left(e^{-(\epsilon^* + \lambda_2^- \lambda_1^j)t} - 1 \right) + \frac{\epsilon^* C_{20}}{\epsilon^* + \lambda_2} e^{-(\epsilon^* + \lambda_2)t} \quad (3.62)$$

– at $t < t_0$, and

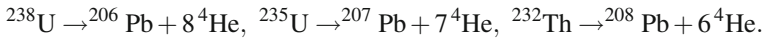
$$C_2 = \frac{1}{\phi} \sum_{j=1}^J \frac{k_j \lambda_1^j C_{10}^j}{(\lambda_1^j - \lambda_2^- \epsilon^*)} e^{-\lambda_1^j t} \left(e^{-(\epsilon^* + \lambda_2^- \lambda_1^j)t_0} - 1 \right) + \frac{\epsilon^* C_{20}}{\epsilon^* + \lambda_2} e^{-(\epsilon^* + \lambda_2)t_0} \quad (3.62a)$$

– at $t \geq t_0$.

Thus, some hydrodynamic characteristics of water-bearing strata systems can be determined by measuring the ratios between the current concentrations of isotopes (parent and daughter) in groundwater and rock. We will exemplify this by a calculation scheme which can be used in studying the distribution in an aquifer of ^4He concentrations as a result of in situ alpha-decay of natural uranium- and thorium-series elements in rocks and sediments.

3.3.4 Basic Concept and Model Development for ^4He Groundwater Dating

The radioactive decay of uranium and thorium results in the formation of a series of isotopes that are radiogenic by themselves and keep disintegrating into stable lead isotopes. These radioactive disintegrations are accompanied by the emission of ^4He atoms (Torgersen and Clarke 1985; Castro et al. 2000). Three such radioactive series exist:



As can be seen, the decay of each atom among ^{238}U , ^{235}U , ^{232}Th results in the emission of $k_1 = 8$, $k_2 = 7$, $k_3 = 6$ atoms of *stable* ($\lambda_2 = 0$) ^4He isotope.

The in situ production rate of ^4He in each of these alpha-decay series is determined by the respective half-lives, and the concentration of uranium and thorium in the rock. If the rate of ^4He solid-to-liquid mass transfer is known, it is possible to use ^4He as a quantitative tracer of groundwater travel times. Thus, stable ^4He is a representative of the age tracers that are produced in the subsurface and accumulate in flowing groundwater.

3.3.4.1 Hydraulically Isolated Aquifer with Solids Producing ^4He

As follows from (3.62) and (3.62a), the substitution in them of the initial concentrations C_{10}^j from (3.61) ($J = 3$) yields (the case of $\epsilon^* = 0$):

$$C_2 = \frac{1}{\phi} \left(k_1 C_1^1 (e^{-\lambda_1^1 t} - 1) + k_2 C_1^2 (e^{-\lambda_1^2 t} - 1) + k_3 C_1^3 (e^{-\lambda_1^3 t} - 1) \right) \text{ at } t < t_0, \quad (3.63)$$

$$C_2 = \frac{1}{\phi} \left(k_1 C_1^1 (e^{-\lambda_1^1 t_0} - 1) + k_2 C_1^2 (e^{-\lambda_1^2 t_0} - 1) + k_3 C_1^3 (e^{-\lambda_1^3 t_0} - 1) \right) \text{ at } t \geq t_0. \quad (3.63a)$$

Here C_1^1, C_1^2, C_1^3 are the initial concentrations of ^{238}U , ^{235}U , ^{232}Th in the rock.

Equations 3.63 and 3.63a and all subsequent relationships can be modified to account for the incomplete helium release from rock into water. To do this, it is sufficient to multiply constants k_i in Eqs. 3.63 and 3.63a by Λ , the fraction of helium produced in the rock that is released into the water.

The ^4He dating method is used for studying water exchange in deep systems of water-bearing strata, whose existence time is measured by geological times, during which the effect of recharge boundaries manifests itself in full measure, i.e., the condition $t \geq t_0$ is almost always valid. The time t_0 in this case is associated with “groundwater age”, i.e., the time interval separating the moment of sampling in the point x and the moment of atmospheric water intrusion into the aquifer in the point $x = 0$ (one-dimensional problem formulation). In the general case it can be found from Eq. 3.63a.

If we take $\lambda_1^j t_0 \ll 1$ ($e^{\lambda_1^j t_0} \approx 1 + \lambda_1^j t_0$), the expressions in parentheses in solution (3.63a) become *linear functions of t_0* , and formula (3.63a) becomes

$$C_2 = \left(\frac{k_1 \lambda_1^1}{\phi} C_1^1 + \frac{k_2 \lambda_1^2}{\phi} C_1^2 + \frac{k_3 \lambda_1^3}{\phi} C_1^3 \right) t_0, \quad (3.64)$$

whence

$$t_0 = \frac{C_2}{P'}, \quad (3.65)$$

where

$$P' = \frac{1}{\phi} (k_1 \lambda_1^1 C_1^1 + k_2 \lambda_1^2 C_1^2 + k_3 \lambda_1^3 C_1^3) \quad (3.65a)$$

is the accumulation rate of radiogenic helium [at $\text{L}^{-1} \text{year}^{-1}$], i.e., when the dimensionless complexes $\lambda_1^j t_0$ is small, ^4He accumulates with an approximately constant rate; $\phi P'$ is the production rate of the radionuclide (Mook 2000).

Formula (3.65) corresponds to a *linear accumulation model*. The model presumes that the isotopes (^4He , in this context) are produced by decay of naturally occurring nuclides (uranium and thorium) with very long half-lives. The decay is slow enough for the parents to be abundant, and hence the rate at which they produce daughter products to be nearly constant. The accumulation with time, then, is essentially linear, and the methods are suitable for dating very old groundwater (Bethke and Johnson 2008).

If the latter condition is valid, the steady (at $t \geq t_0$) distribution of ^4He in a single-layer system with $q_x = q = \text{const}$, $\epsilon_u = 0$, $\lambda_2 = 0$, $C \equiv C_2$ (^4He concentration in water), can be described by the differential equation

$$qm \frac{\partial C}{\partial x} - m \phi P' = 0, \quad (3.66)$$

which is a kind of generalization of the system of Eqs. 3.60; it is of use in the analysis of ^4He accumulation in multilayer systems (see below).

3.3.4.2 A Multilayer Flow System with Upward Diffusion of Earth Crust/Mantle ^4He

Numerous studies show that the models considered above significantly overestimate the age of groundwater (Torgersen and Clarke 1985; Castro et al. 2000; Aggarwal et al. 2004; Bethke and Johnson 2008; Kulongoski et al. 2008). This is due to the inflow of ^4He from large depth, increasing its concentration in the aquifer relative to the values that could be expected based on the hypothesis of its production exclusively because of the decay of ^{238}U , ^{235}U , ^{232}Th nuclei. The other source of extraneous helium is the diffusion of He out of the confining strata.

The isotope is produced throughout Earth's crust or mantle and must ultimately escape upward. The magnitude of deep helium flux, J_0 , associated with the decay of radioactive elements of Earth's crust, can reach the values varying within $(N \cdot 10^{-7} \div N \cdot 10^{-6}) \text{ cm}^3 \text{STP } ^4\text{He cm}^{-2} \cdot \text{year}^{-1}$ (Stute et al. 1992; Castro et al. 2000; Aggarwal et al. 2004; Kulongoski et al. 2005; Kulongoski et al. 2008). ^4He flux from the Earth into the atmosphere is 10^6 at $\text{cm}^{-2} \text{c}^{-1}$ multiplied by a factor varying from several tenths to a few units.

Let us derive a system of mass balance equations for ^4He isotope in a multilayer system, assuming that the rate of its generation (P'_i) during the decay of parent products is constant (3.66) in any i th layer, and the concentration distributions C_i are steady (this is true when $t \geq t_0$):

$$\begin{aligned} q_1 m_1 \frac{\partial C_1}{\partial x} - m_1 \phi_1 P'_1 - J_0 + J_1 &= 0, \\ q_2 m_2 \frac{\partial C_2}{\partial x} - m_2 \phi_2 P'_2 - J_1 + J_2 &= 0, \\ &\dots\dots\dots, \\ q_i m_i \frac{\partial C_i}{\partial x} - m_i \phi_i P'_i - J_{i-1} + J_i &= 0, \end{aligned} \quad (3.67)$$

where the interlayer fluxes, J_i , are determined by concentration gradients:

$$J_1 = \frac{D_e}{m_{01}} (C_1 - C_2), J_2 = \frac{D_e}{m_{02}} (C_2 - C_3), \dots, J_i = \frac{D_e}{m_{0i}} (C_i - C_{i+1}); \quad (3.67a)$$

here q_i is the horizontal Darcy velocity; D_e is the effective diffusion coefficient of ^4He ; m_i and m_{0i} are the thicknesses of the high- and low-permeability layers. According to the model under consideration, ^4He accumulates in groundwater flowing through the stratified system owing to its release only from the aquifer solids and it is assumed that the bounding impervious layers (aquitards), separating aquifers, are not sources of ^4He themselves.

With the expressions for mass fluxes (3.67a) substituted into the balance Eqs. 3.67, the latter becomes

$$\begin{aligned}
 q_1 \frac{\partial C_1}{\partial x} - \phi_1 P'_1 - J_0/m_1 + \alpha_1(C_1 - C_2) &= 0, \\
 q_2 \frac{\partial C_1}{\partial x} - \phi_2 P'_2 - \alpha_1(C_1 - C_2) + \alpha_2(C_2 - C_3) &= 0, \\
 \dots\dots\dots, \\
 q_i \frac{\partial C_1}{\partial x} - \phi_i P'_i - \alpha_{i-1}(C_{i-1} - C_i) + \alpha_i(C_i - C_{i+1}) &= 0,
 \end{aligned} \tag{3.68a}$$

where

$$\alpha_i = D_e / m_{0i} m_i \tag{3.68b}$$

is the interlayer exchange factor. The system of equations can be solved numerically (see 3.4.4.3 below) with the boundary conditions

$$C_i(x=0) = 0. \tag{3.69}$$

3.3.5 Converting Physical Units

The basic concentrations C_1 (or C_1^j) and C_2 in the relationships considered above are measured in terms of the *number of atoms* subject to decay per unit volume of solution or rock. However, more common in the practical analysis of concentration distributions is the use of other units.

The concentration of tritium [^3H] in laboratory analyses of water samples used for *tritium* or *tritium-helium-3 dating methods* is most often given in tritium units, T.U. (1 T.U. = 1 atom of ^3H per 10^{18} atoms of ^1H = $1.1 \cdot 10^{-19}$ mol g $^{-1}$ H_2O = 66846 at g $^{-1}$ H_2O = 0.118 Bq L $^{-1}$).

The concentration of dissolved helium [^3He] is measured in volumetric units cm ^{3} STP g $^{-1}$ H_2O . The conversion of T.U. into the same measurement units can be made by the formula

$$1 \text{ cm}^3 \text{STP g}^{-1} \text{H}_2\text{O} = \frac{4.0193 \cdot 10^{14}}{(1 - S/1000)} \text{T.U.},$$

where S is salinity ($^0/_{00}$). Therefore

$$\begin{aligned}
 [^3\text{He}](\text{cm}^3 \text{STP g}^{-1} \text{H}_2\text{O}) &= \frac{(1 - S/1000)}{4.0193 \cdot 10^{14}} \frac{[^3\text{H}]_{10}}{(1 + \bar{\epsilon})} [\bar{\epsilon} e^{-(1+\bar{\epsilon})\bar{r}} - (1 + \bar{\epsilon}) e^{-\bar{\epsilon}\bar{r}} + 1], \\
 \bar{C}_{21} = \frac{C_2}{C_1} &= \frac{4.0193 \cdot 10^{14}}{(1 - S/1000)} \frac{[^3\text{He}]}{[^3\text{H}]}.
 \end{aligned}$$

The *helium-4 dating method* involves measuring the volumetric concentration of dissolved ^4He C_2^V ($\text{cm}^3\text{cm}^{-3}\text{H}_2\text{O}$ or $\text{cm}^3\text{STP g}^{-1}\text{H}_2\text{O}$) and the weight concentration of parent isotopes ^{238}U , ^{235}U and ^{232}Th , $C_1^{j,W}$ (g/g aquifer solids) in solution (groundwater samples).

To convert the measurement units, we will use the following relationships between the amount of the matter, its molecular mass, and volume.

The atomic concentration C_2 ($\text{atL}^{-1}\text{H}_2\text{O}$) is related to the molar concentration C_2^M by:

$$C_2^M = C_2/N_A \text{ (in molL}^{-1}\text{H}_2\text{O)},$$

where $N_A = 6.02205 \cdot 10^{23} \text{ at mol}^{-1}$ is *Avogadro number*. Now the physical volume of dissolved ^4He (C_2^V) becomes

$$C_2^V = C_2^M V_m \text{ (in LL}^{-1}\text{H}_2\text{O)},$$

where $V_m = 22.415 \text{ L mol}^{-1}$ is the molar volume (the volume of one mole). Now

$$C_2 = (C_2^V/V_m)N_A \quad \text{or} \quad C_2^V = (V_m/N_A)C_2.$$

The volumetric concentration of an isotope in rock $C_1^{j,V}$ (in g/(L rock matrix)) can be converted into the molar concentration $C_1^{j,M}$ by the formula

$$C_1^{j,M} = C_1^{j,V}/M_1^j \text{ (in mol/L rock matrix)},$$

where M_1^j is the molecular weight of the j th isotope. For the relationship between $C_1^{j,M}$ and the atomic concentration C_1^j , we have

$$\begin{aligned} C_1^j &= C_1^{j,M} N_A \text{ (in at/L of rock matrix), or} \\ C_1 &= (C_1^{j,V}/M_1^j)N_A \text{ (in at/L of rock matrix)}. \end{aligned}$$

At the same time, the concentration $C_1^{j,V}$ is related with radionuclide concentration, expressed in weight units per unit weight of aquifer solids ($C_1^{j,W}$), by the formula

$$C_1^{j,W} = C_1^{j,V}/\rho_b 10^3 (1 - \phi) \text{ (in g/g)},$$

where ρ_b is rock density (in g cm^{-3}), ϕ is rock porosity. Now

$$C_1 = \left(N_A \rho_b 10^3 (1 - \phi) / M_1^j \right) C_1^{j,W} \text{ (in at/L of rock matrix)},$$

$10^3 [\text{cm}^3\text{L}^{-1}]$ is a factor for density conversion from g cm^{-3} into g L^{-1} .

Table 3.1 Data for evaluating the accumulation rate of radiogenic helium

j	Isotope	k_j	M_1^j , g mol ⁻¹	λ_1^j , year ⁻¹
1	²³⁸ U	8	238	$1.5513 \cdot 10^{-10}$
2	²³⁵ U	7	235	$9.8485 \cdot 10^{-10}$
3	²³² Th	6	232	$4.9750 \cdot 10^{-11}$

Thus, formula (3.65) for groundwater age becomes

$$t_0 = \frac{C_2^V}{P}, \quad (3.70)$$

$$P = \frac{(1-\phi)}{\phi} \frac{k_1 \lambda_1^1 V_m \rho_b 10^3}{M_1^1} C_1^{1,w} + \frac{(1-\phi)}{\phi} \frac{k_2 \lambda_1^2 V_m \rho_b 10^3}{M_1^2} C_1^{2,w} + \frac{(1-\phi)}{\phi} \frac{k_3 \lambda_1^3 V_m \rho_b 10^3}{M_1^3} C_1^{3,w}. \quad (3.70a)$$

Substitute parameter values form Table 3.1 into formula (3.70a). The result will be

$$P = 0.1169 \frac{(1-\phi)}{\phi} C_1^{1,w} \rho_b 10^{-6} + 0.659 \frac{(1-\phi)}{\phi} C_1^{2,w} \rho_b 10^{-6} + 0.0288 \frac{(1-\phi)}{\phi} C_1^{3,w} \rho_b 10^{-6}, [\text{cm}^3 \text{cm}^{-3} \text{H}_2\text{O yr}^{-1}]. \quad (3.70b)$$

If C_2^V is measured in $\text{cm}^3 \text{STPg}^{-1} \text{H}_2\text{O yr}^{-1}$, the formula for generation rate P takes a different form

$$P = 0.1169 \cdot C_1^{1,w} \frac{\rho_b (1-\phi)}{\phi \rho_{\text{H}_2\text{O}}} 10^{-6} + 0.659 \cdot C_1^{2,w} \frac{\rho_b (1-\phi)}{\phi \rho_{\text{H}_2\text{O}}} 10^{-6} + 0.0288 \cdot C_1^{3,w} \frac{\rho_b (1-\phi)}{\phi \rho_{\text{H}_2\text{O}}} 10^{-6}, [\text{cm}^3 \text{STPg}^{-1} \text{H}_2\text{O yr}^{-1}], \quad (3.70c)$$

$\rho_{\text{H}_2\text{O}}$ is groundwater density (gcm^{-3}).

Experts in isotopic hydrogeology more commonly use the formula (Andrews and Lee 1979; Kulongoski et al. 2008)

$$P = \frac{1-\phi}{\phi} \rho_b \Lambda \{ 1.19 \cdot 10^{-13} [\text{U}] + 2.88 \cdot 10^{-14} [\text{Th}] \}, \quad (3.70d)$$

which does not distinguish among the concentration of different uranium isotopes; here P is ^4He production rate ($\text{cm}^3 \text{STPg}^{-1} \text{H}_2\text{O yr}^{-1}$); $[\text{U}]$ and $[\text{Th}]$ are the uranium and thorium concentrations in the aquifer solids (ppm); 1.19×10^{-13} and 2.88×10^{-14} ($\text{cm}^3 \text{STPg}^{-1} \text{yr}^{-1} \mu\text{g}^{-1}$ natural U and Th) are ^4He production rates for

U and Th series in equilibrium with their decay products; Λ is the fraction of helium produced in the rock that is released into the water (assumed to be unity).

The rate of helium accumulation, P , for medium-activity rocks, as evaluated by V.P. Savchenko, a founder of the method (1936), was $3.4 \cdot 10^{-12} \text{ cm}^3 \text{cm}^{-3} \text{H}_2\text{O year}^{-1}$. Indeed, this value falls in the range of characteristic $P = 10^{-12} - 10^{-11} \text{ cm}^3 \text{cm}^{-3} \text{H}_2\text{O year}^{-1}$, which is given in later publications (Castro et al. 2000; Aggarwal et al. 2004). The mean (background) uranium concentrations in rocks are $(1-3) \cdot 10^{-6} \text{ gg}^{-1}$ (or 1–3 ppm), thorium concentrations are commonly several times less.

3.4 Hydrodynamic Interpretation of Isotopic Groundwater Monitoring Data: Case Studies

3.4.1 On Groundwater Dating Using Global Isotopes

The issue of specification of the hydrodynamic conditions of groundwater flow and migration, as well as groundwater vulnerability assessment with the use of data on the distribution of global tracers in the subsurface hydrosphere, including radioactive isotopes, is the focus of many studies, whose number increases every year (Clark and Fritz 1997; Mook 2000; Edmunds 2005; Mazor 2004; Hinsby 2007; Bethke and Johnson 2008, and many others). In most such studies, the isotopic data are interpreted in the context of groundwater dating.

There is a classical definition for *the age of a water parcel*: this is the time that has elapsed since it entered the system, which can be called the *residence time* (Etcheverry and Perrochet 2000). This is a good definition in case where the flow system is simple, e.g. advection-only flow system with insignificant mixing and dispersion. However the age of a *groundwater sample* cannot be characterized by a single number, because the sample may consist of a mixture of numerous fractions with different ages. Thus, if mixing (and/or dispersion) occurs, the age of a water sample is a stochastic variable described by a probability density function (Etcheverry and Perrochet 2000; Cornaton and Perrochet 2006; Hinsby 2007; Kazemi et al. 2006; see also Sects. 3.1.3 and 4.2.2).

Groundwater age in the zone of active water exchange is most often evaluated by using observational data on the distribution of one or several global tracers, such as tritium ^3H (currently it is often used in combination with its decay product, ^3He), ^{14}C , ^{36}Cl , ^{85}Kr , SF_6 (sulfur hexafluoride), and chlorofluorocarbon compounds CCl_3F (shortly, CFC-11) and CCl_2F_2 (CFC-12), as well as $\text{C}_2\text{Cl}_3\text{F}_3$ (CFC-113) (Fig. 3.6).

^3H , ^{14}C , ^{36}Cl , ^{85}Kr in the atmosphere originate from nuclear tests, uranium industry, and nuclear power engineering. Nuclear weapon tests in the 1950s to mid 1960s released to the atmosphere certain radionuclides notable because they form a “bomb pulse”, a period during which groundwater recharge was rich in the isotopes.

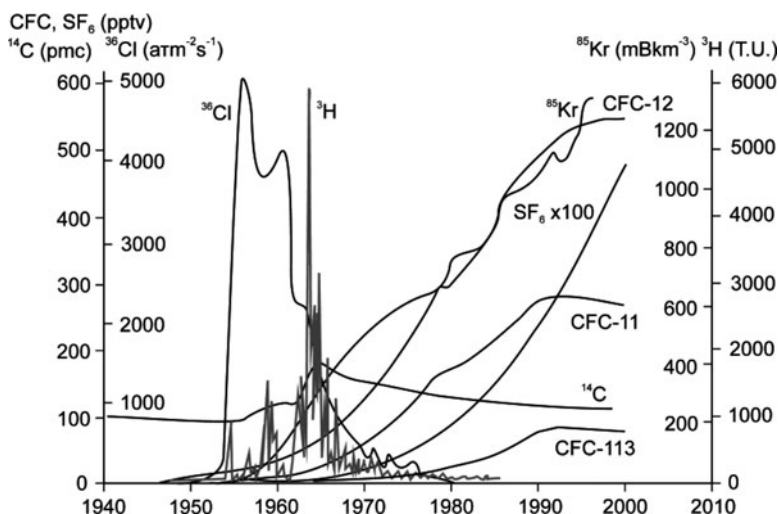


Fig. 3.6 Time variations in global tracer concentrations in the atmosphere (1940–2000) (Hinsby 2007). Pmc is carbon percentage concentration relative to the present-day level (up to 1950), pptv is 10^{-12} (one trillionth of the volume) (Reprinted by permission of the publisher, Leibniz-Institute for Applied Geosciences, GGA–Institute)

After atmospheric testing was banned, the isotopes diminished in concentration as they mixed into the oceans and subsurface, and, if short-lived, decayed (Clark and Fritz 1997; Bethke and Johnson 2008). ^3H , ^{36}Cl , and ^{14}C track water movement and are well suited as age tracers. Groundwater enriched in the isotopes could have recharged only during the bomb pulse and hence is known to have an age falling within a bracketed range. Assigning a more specific age to a sample can be complicated, however, because an observed concentration matches two points in time, one on the rising and one on the falling limb of the pulse (Bethke and Johnson 2008). It was also noted (Han et al. 2006) that, because of the multiple peaks in ^3H content of precipitation (Fig. 3.6), interpretation of an observed concentration of ^3H can result in multiple possible years of recharge.

The development of chemical industry is associated with the first release of chlorofluorocarbon compounds which have no natural sources at all. Among the manufactured gases, chlorofluorocarbon compounds, or CFCs, and sulfur hexafluoride, SF_6 , have proved useful for age dating (Plummer 2005; Busenberg and Plummer 2006, 2008; Plummer and Busenberg 2006). The various CFC compounds have different histories (Fig. 3.6). Some increased in concentration early and then leveled off as they were banned from use. Others have accumulated more recently (Cook et al. 1995). The concentration in groundwater of one of the manufactured compounds, then, generally maps to a unique sample age (Bethke and Johnson 2008).

If atmospheric precipitation is considered as the original carrier of the above isotopes and CFCs in groundwater, it should be mentioned that (i) the concentration of each indicator in infiltration water is a complex function of time; (ii) the

shape of such concentration function in each geographic point is individual and may vary appreciably, though obeying the general trends in global distribution, so the resulting estimates can feature considerable bias, unless detailed many-year data on the composition of atmospheric precipitation are available; (iii) all calculations, except for dating based on ^3H data, require additional geochemical considerations (corrections), since the equilibrium isotope concentrations in the atmospheric and pore waters can be different (due to variations in the chemistry, temperature, and pressure).

Unlike ^3H , ^{36}Cl , and ^{14}C , the concentrations of ^{85}Kr and chlorofluorohydrocarbons steadily increased until the early 1990s (Smethie et al. 1992; Goode et al. 1999), and the CFC-11/CFC-12 remained approximately constant since 1975 (Ekwurzel et al. 1994). Since the mid-1990s, CFC concentrations in atmospheric water were relatively stable or even slightly decreased (Goode et al. 1999).

^{85}Kr ($T_{1/2} = 10.76$ yr) is released during the operation of nuclear reactors, and its concentration in the atmosphere has increased in a nearly linear fashion over the past several decades (Smethie et al. 1992; Han et al. 2006). Accordingly, an ^{85}Kr concentration measured in groundwater matches a unique age, when radioactive decay is taken into account (Bethke and Johnson 2008). Another advantage of ^{85}Kr is that it is an inert gas, whose concentrations in natural water are very low.

Conversely, chlorofluorohydrocarbons are subject, to one extent or another, to anaerobic microbial degradation (according to different estimates, $T_{1/2}$ varies from several tens to 100–130 years) (Ekwurzel et al. 1994; Happell et al. 2003; Kresic 2007), whose rate depends on many natural factors; sorption interaction between CFC and rock was also found to occur (Reilly 1994). Equilibrium CFC concentration near groundwater surface at given temperature can be evaluated by the available values of their concentrations in precipitation.

^{85}Kr , SF_6 and chlorofluorocarbon compounds, as gases, rapidly migrate in the interstitial air in the aeration zone under the effect of diffusion. Because of this, they reach phreatic water surface in a shorter time than the isotopes dissolved in atmospheric water (Zoellmann et al. 2001). The ensuing difference becomes significant from the viewpoint of possible errors in the interpretation of observational data when the aeration zone thickness exceeds several tens of meters.

Radioactive carbon ($T_{1/2} = 5568$ yrs) is most sensitive to carbonate equilibria and some exchange processes in the water-rock system, therefore the corresponding dating should be accompanied by special thermodynamic calculations.

Finally, owing to the progress in analytical methods (Tosaki et al. 2007) it became possible to trace groundwater migration with the use of the long-lived ^{36}Cl isotope ($T_{1/2}$ of about 301,000 years). Its global peak (Fig. 3.6), exceeding the background concentrations by almost 1000 times is also due to nuclear tests and was recorded in the late 1950s–early 1960s, i.e., the peak values of ^{36}Cl were recorded somewhat earlier than the maximal concentrations of ^3H .

The interpretation of data on the distribution of global isotopic tracers is often based on analytical models with generalized (lumped) parameters, largely inheriting the features of black-box models, used to describe processes in chemical industry

(Zuber 1986; Maloszewski and Zuber 1993; Zuber et al. 2000). The progress in mathematical modeling methods considerably extended the capabilities of isotopic data interpretation (Mattle et al. 2001; Zoellmann et al. 2001), with the result that numerical modeling is gradually replacing analytical methods in processing this type of data. However, in our opinion, the potentialities of analytical methods, which explicitly describe the transport processes and nuclear transformation reactions (Sects. 3.2 and 3.3), have not been exhausted.

3.4.2 *Calculated Distributions of Atmospheric ^3H and Its Decay Product ^3He in Groundwater (Typical Curves)*

The global radioactive pollution of the air is due to nuclear tests in the period 1945–1980. According to expert estimates (Makhonko 2002), the atmospheric tests can be assumed to include 525 nuclear explosions with a total yield of 439 Mt. Moscow Treaty Banning Nuclear Weapon Tests in the Atmosphere, in Outer Space and under Water was signed at Moscow in 1963. Despite the fact that France and People's Republic of China did not join the Treaty until 1980, gradual self-purification from radioactive products of nuclear explosions was found to take place in the atmosphere since the mid-1960s. Such products can be regarded as high-efficiency global tracers in studying atmospheric phenomena and water exchange in the subsurface hydrosphere.

3.4.2.1 Basic Function

Large-scale nuclear testing caused a global rise in anthropogenic tritium in atmospheric waters (Fig. 3.7). Intense tritium pollution of atmospheric water could be seen to persist and increase until the mid-1960s. Next, after the cessation of mass testing of nuclear facilities in the atmosphere, tritium concentrations started gradually decreasing to reach by now (about 60 years after the beginning of tests) the values as low as several times the background level. The present-day mean tritium concentration is 7–10 T.U. (the Northern Hemisphere) and about 2 T.U. (the Southern Hemisphere) (Edmunds 2005). This fact contributed to the development of isotopic methods aimed at studying the dynamics of groundwater flow in hydrogeological systems, in particular, groundwater dating.

Systematic observations of tritium concentration in atmospheric precipitation at Hydrometeoservice network in USSR territory started in mid-1969 (Fig. 3.8a). It can be easily seen that the function $[^3\text{H}](t)$ in the plot of mean data for the USSR (Fig. 3.8a), obtained in 1970–1995, is very similar to the plot 1 of the same type in Fig. 3.7 constructed based on observational data from Ottawa, Canada.

For the sake of comparison, Fig. 3.8b gives the dynamics of variations in ^{137}Cs concentration in the near-surface air layer (Makhonko 2002). Moreover, Fig. 3.8 gives data on the intensity of atmospheric fallouts of these radionuclides onto land surface. As follows from the comparison of Fig. 3.8a, b, the Chernobyl accident in

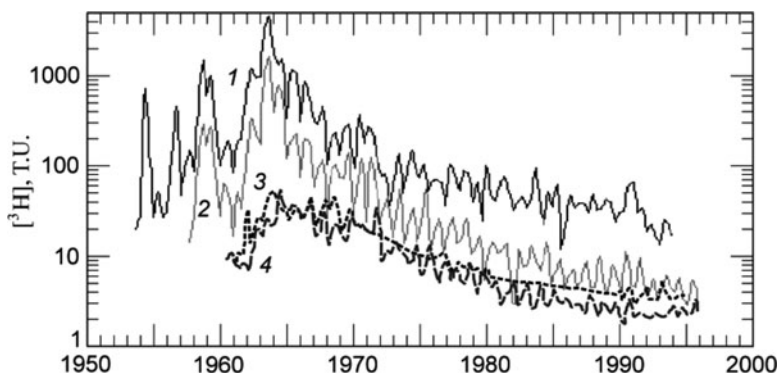


Fig. 3.7 Tritium concentration in atmospheric precipitation by four IAEA stations (1953–1996). (1) Ottawa, Canada (Northern Hemisphere, continent), (2) Valencia, Ireland (Northern Hemisphere, sea), (3) Harare, Zimbabwe (Southern Hemisphere, continent), (4) Kaitoke, New Zealand (Southern Hemisphere, sea). IAEA/WMO data 1998. The difference between the pollution intensity between atmospheric waters of the two hemispheres is due to the existence of the equatorial convergence zone of air flows, which hamper the passage of explosion products from the Northern into the Southern Hemisphere

1986¹, which had a strong impact on the atmospheric pollution by ^{137}Cs and other anthropogenic radionuclides, did not affected the mean monthly tritium concentration in sediments and the rate of its fallout from the atmosphere.

^3H concentration in sediments and the specific rate of its deposition vary during the year in the same manner as in the case of ^{137}Cs and other nuclear explosion products released into the atmosphere (Fig. 3.8). In particular, a distinct rise in ^3H concentration can be seen every year after the spring changes in the tropopause height because of the tritium that have accumulated in the stratospheric reservoir and then enters the troposphere whence it reaches the land surface with precipitation. Because of the gradual depletion of anthropogenic ^3H reserves in the stratosphere, notwithstanding the periodic injections, the amplitude of seasonal variations in its concentration gradually decreases over the years (Makhonko 2002).

3.4.2.2 Response Functions

Hereafter, the basic input function characterizing long-term variations in tritium concentration in infiltration water [$C_R = f(t)$], will be taken to be the function in Fig. 3.7 (curve 1), associated with the most representative observational series and approximated by us by a step-wise plot (Fig. 3.9). We suppose also that atmospheric water infiltration with a rate of ε takes place uniformly over the entire drainage

¹ According to some estimates, the radionuclides released from the failed block of NPP had the total activity of up to 50 Mci (3–4% of the original amount of radionuclides in the reactor).

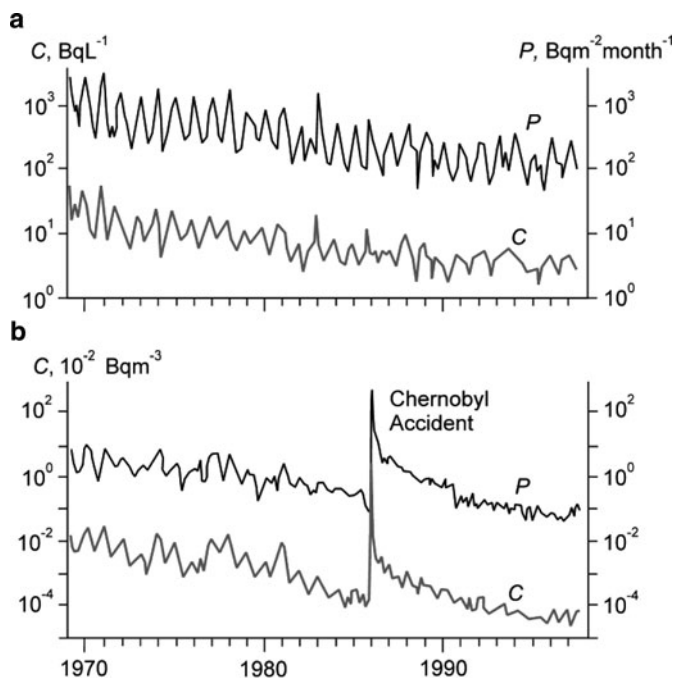


Fig. 3.8 Time variations in mean monthly concentrations, C , of (a) ^3H in atmospheric precipitation and (b) ^{137}Cs in the air combined with plots of variations in the specific deposition rate of these radionuclides (P) from the atmosphere in USSR territory (Makhonko 2002). $1 \text{ Bq} = 8.47 \text{ T.U.}$ Marks on the abscissa correspond to the mid-summer of each year

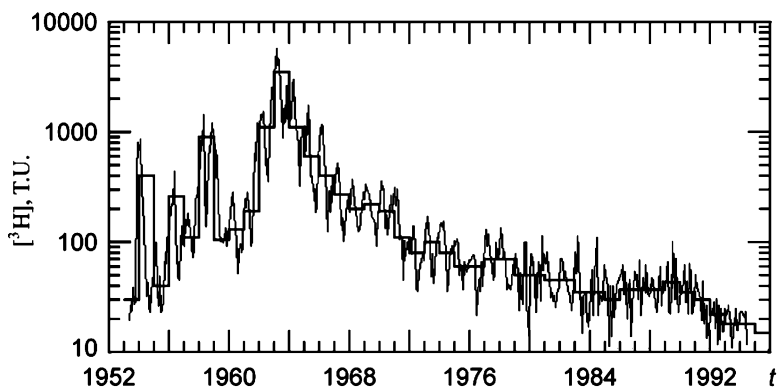


Fig. 3.9 Approximation of the plot of $[^3\text{H}]_R(t)$ by a step-wise function. Ottawa, Canada (mean monthly data)

area (Fig. 3.1, $Q_0 = 0$), and tritium residence time in the aeration zone is not too large. The values used in calculations will be $T_{1/2} = 12.264 \text{ yr}$ and $\lambda = 0.0565 \text{ yr}^{-1}$ (Akulov and Mamyrin 2004).

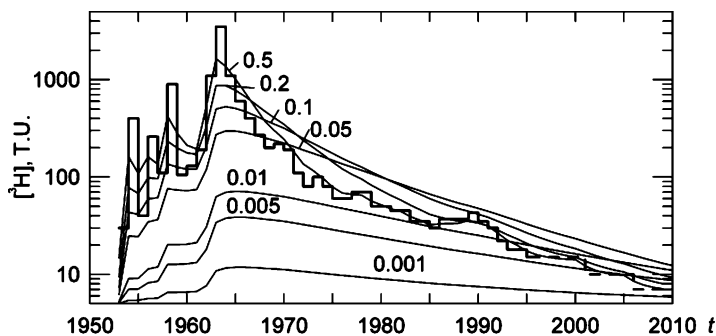


Fig. 3.10 Mean annual tritium concentrations in atmospheric water (the thick broken line is for data from Ottawa station, Canada) and response curves at different values of parameter $\epsilon^* = \epsilon/m\phi = \tau_0^{-1}$, year^{-1}

^3H concentration distribution. The mean concentration of ^3H (C) in the aquifer in the given time at the step-wise input function is determined by the solution (3.23), which is a superposition of the basic solution $C = F(t)$ (see 3.21, the first equation). Calculation by (3.23) for the characteristic range of variations in the complex parameter $\epsilon^* = \epsilon/m\phi$, year^{-1} ($0.001 < \epsilon^* < 0.5$, corresponding to the characteristic turn-over time $2 < \tau_0 < 1,000$ year), yielded the concentration distributions given in Fig. 3.10. The absolute values of C were evaluated at $C^0 = 5 \text{ T.U.}$ (the background level before 1953); extrapolated values were used for 1996–2010.

Theoretically, it can be seen that nowadays (the early 2000s), tritium concentration in groundwater should vary within a very narrow range from a few units to 10–15 T.U.² Of interest is also the fact that tritium concentration in atmospheric precipitation can exceed its concentration in groundwater (measurements made at the same time are meant here). Overall, the analysis of the graphical solution (Fig. 3.10) suggests that the peak in the sensitivity of curves recorded in the 1960s–1970s has already passed. Curves with different values of parameter ϵ^* intersect in the plot, which hampers the processing of observational data obtained from individual measurements and makes the estimate of this complex parameter extremely unreliable, as well as the estimate of the mean age τ_0 associated with it. Even though ^3H concentrations may not be suitable for precise age determinations, the ^3H data are invaluable when combined with the study of other global tracer concentration distributions (Han et al. 2006).

^3He concentration distribution. The necessary calculations can be based on the basic solution (3.42), in which $C_{10} \equiv [^3\text{H}]_{10}$ is the original concentration (at time $t = 0$) of the parent radionuclide, i.e., tritium. To account for the time variations in tritium concentration in infiltration water $[^3\text{H}]_R = f(t)$, represented by the plot

² Actually, interval sampling of groundwater can also yield higher tritium concentrations ($> 20 \text{ T.U.}$), which are due to its vertical differentiation in the groundwater flow, which will be discussed below (see Sect. 4.2.3).

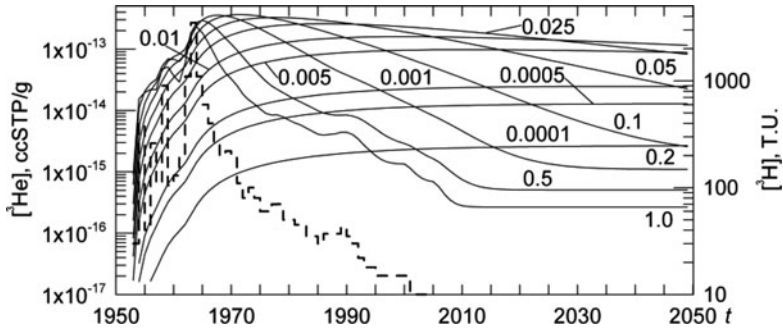


Fig. 3.11 Plots of function $[^3\text{He}](t)$ (full lines) at different $\varepsilon^* = \varepsilon/m\phi = \tau_0^{-1}$, y^{-1} (figures at curves). Dashes show the plot of the input function $[^3\text{H}]_R(t)$ (the right axis of the plot)

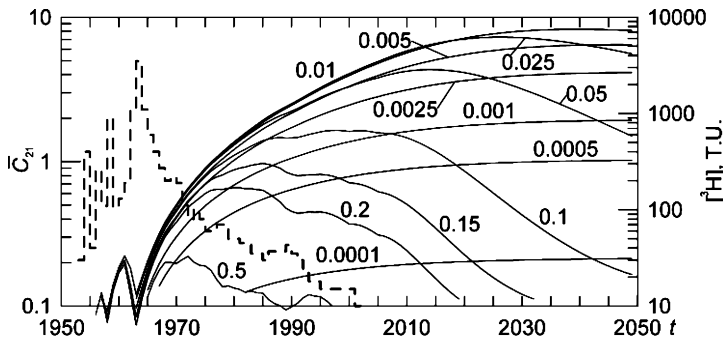


Fig. 3.12 Plots of function $[^3\text{He}]/[^3\text{H}] = f(t)$ (solid line) at different $\varepsilon^* = \varepsilon/m\phi = \tau_m^{-1}$, y^{-1} (figures at curves). Dashes show the plot of input function $[^3\text{H}]_R(t)$ (the right axis of the plot)

in Fig. 3.9, the solution (3.42) should be generalized to the case of step-wise input function by superposition method. Thus, we have the graphic representation of function $C_2 \equiv [^3\text{He}]$ (Fig. 3.11). The curves $\bar{C}_{21} \equiv [^3\text{He}]/[^3\text{H}] = f(t)$ are also easy to calculate (Fig. 3.12).

As can be seen, at small $\varepsilon^* (< 0.025 \text{ year}^{-1})$, curves $[^3\text{He}](t)$ and $\bar{C}_{21}(t)$ increase monotonically in the period under consideration (1950–2050), i.e., ^3He is accumulating in the aquifer systems. Clearly, water exchange in such systems is slowed, such that the recorded ^3He concentrations agree with the mean water residence time (τ_0) of more than 40 years. In systems with more active water exchange ($\varepsilon^* > 0.025 - 0.05 \text{ yr}^{-1}$, $\tau_0 < 20 - 40 \text{ yr}$), the plots of $[^3\text{He}](t)$ (Fig. 3.11) and $\bar{C}_{21}(t)$ (Fig. 3.12), in accordance with forecasts of the model considered, should have extreme character within the time range in question. The peak values of $[^3\text{He}]$ fell on the late 1960s–early 1970s, so that ^3He concentration in such system should be gradually decreasing now.

The branches of curves $\bar{C}_{21}$, constructed for different ε^* , can be both ascending and descending as well. It is important that the plots of reduced concentrations $\bar{C}_{21} = [^3\text{H}]/[^3\text{He}] = f(t)$ (Fig. 3.12) are more sensitive to the variability of parameter ε^* (τ_0) than the plots of function $[^3\text{H}](t)$ considered above (Fig. 3.12). This makes

the use of tritium-helium-3 method promising for studying aquifer systems. The uncertainty arising from the intersection of curves with different ages can be eliminated by involving additional hydrological data. Finally, it should be mentioned that the commonly accepted opinion that the $[\text{He}]/[\text{H}]$ ratio does not depend on the form of the input function $[\text{H}]_R(t)$ appears to be erroneous.

3.4.3 A Case History of ^3H – ^3He Groundwater Analysis and Data Interpretation (Izhora Plateau, Leningrad Region, Russia)

Izhora Plateau is a unique natural groundwater reservoir of infiltration genesis. It is located in the southern Leningrad province, 15–25 km from the Gulf of Finland, and is separated from the sea by Predglint Lowland (Fig. 3.13). The study region is adjacent to the zone of Nuclear-Industrial Center (the NPP is a potential source of groundwater pollution at the regional scale and nuclear waste facilities form local sources), which is of specific interest in the context of detailed studying of hydrological processes, in particular, contaminant migration in groundwater (see Chaps. 21 and 22).

The geological section is represented by low-thickness (no more than 15 m) sandstones of Upper Cambrian and limestones (60–100 m in thickness) of Ordovician. The aquifers associated with these rocks and having the same names are very water-abundant, especially the Ordovician. Its transmissivity is very high, reaching several thousands of square meters per day, mostly because of rock karstification. The active infiltration of atmospheric precipitation forms a dome-like structure of groundwater flow with radial symmetry (Fig. 3.13). The mean specific infiltration rate, ϵ , estimated by different methods, is about $4 \cdot 10^{-4}$ m/day.

At the same time, the active interaction between atmospheric and subsurface water makes the latter very vulnerable to different types of pollution. Therefore, the assessment of parameters governing migration processes is an important hydrogeological problem for this region.

The area of isotopic studies is located in the Izhora River basin. The area contains a water intake for the Saint Petersburg Institute of Nuclear Physics (SPINP), which drains the Ordovician aquifer (with a mean rate of about 6,600 m³/day). From the engineering viewpoint, the water intake comprises 11 wells spaced 250–300 m apart with the distance of 1,300 m between the extreme wells.

^3H and ^3He isotope concentrations were determined in all wells and the $^3\text{He}/^4\text{He}$ and $^{20}\text{Ne}/^4\text{He}$ ratios were calculated. This made it possible to determine the contribution of ancient water (in particular, containing abyssal ^3He), squeezed out from underlying clay deposits, to the total water balance of the water intake. This contribution never exceeded 0.5%.

The results of sampling were used to evaluate the mean concentrations of the radionuclides in question:

$$[\text{He}] = 7.94 \cdot 10^{-14} \text{ cm}^3 \text{ STP g}^{-1} \text{ H}_2\text{O} \text{ and } [\text{H}] = 29 \text{ T.U.} = 7.22 \cdot 10^{-14} \text{ cm}^3 \text{ g}^{-1}.$$

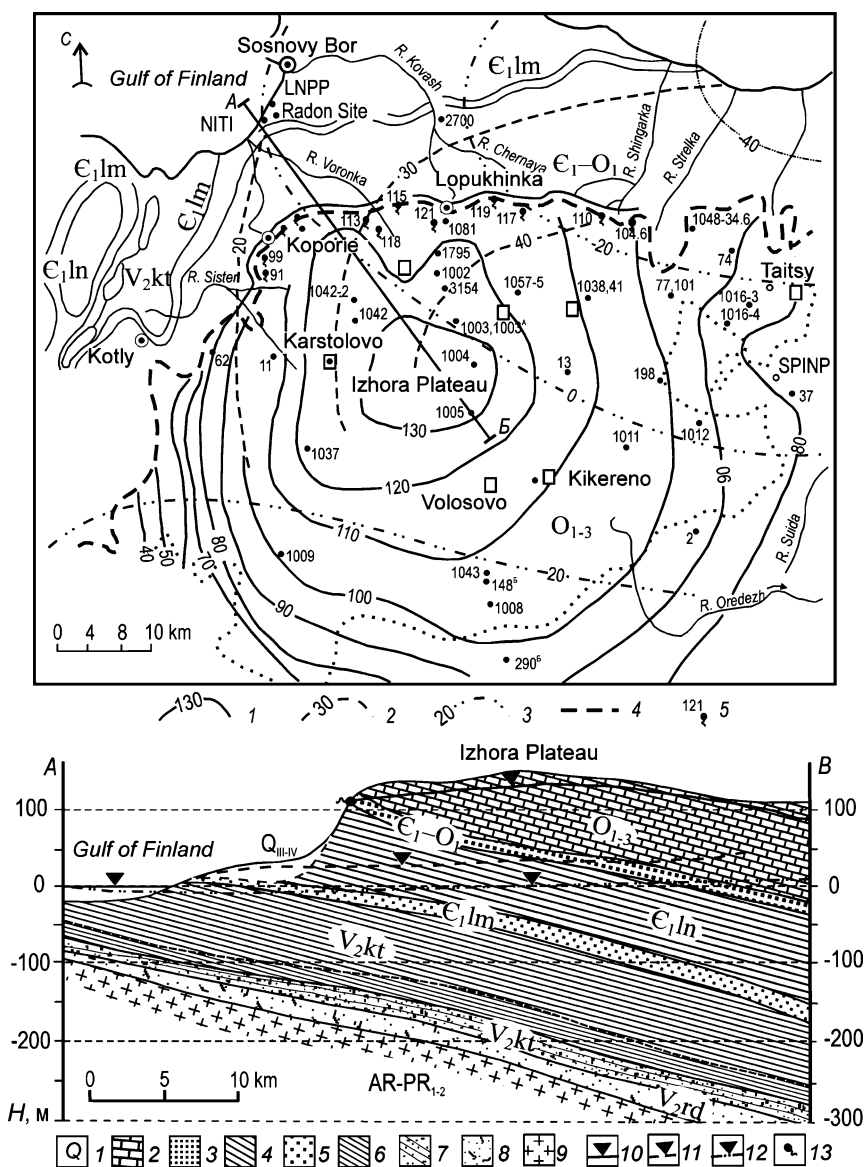
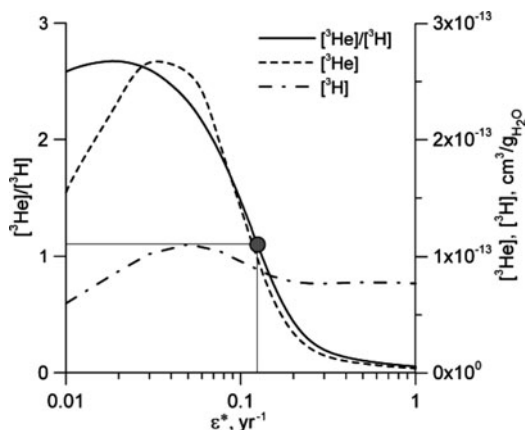


Fig. 3.13 General hydrogeological scheme of the region (Izhora Plateau and Predglint Lowland) and a schematic section along A-B line. In the scheme: (1, 2 and 3) hydroisohypses and piezometric contours: (1) Ordovician aquifer, O₁₋₃, (2) Lower Cambrian (Lomonosovsky) aquifer, E₁lm, (3) Vendian aquifer system, V₂kt – V₂rd; (4) glint line; (5) spring. In the hydrogeological section: *Aquifers and aquifer systems*: (1) Quaternary, Q_{III-IV} aquifer; (2) Ordovician aquifer, O₁₋₃; (3) Lower Cambrian-Ordovician aquifer, E₁-O₁; (5) Lower Cambrian (Lomonosovsky) aquifer, E₁lm; (7) Vendian aquifer system, V₂kt – V₂rd; (9) Archean-Proterozoic water system, AR-PR₁₋₂; (10–12) groundwater level: (10) Ordovician aquifer, (11) Lower Cambrian (Lomonosovsky) aquifer, (12) Vendian (Kothlin and Redkinsky) aquifer system; (13) spring. *Aquicludes*: (4) Lower Cambrian (Lontovaskaya suite, “Blue Clay”), E₁ln; (6) Upper Vendian (Kothlinskaya suite, “Kothlin Clay”), V₂kt

Fig. 3.14 Plot for assessing the complex parameter ε^* . The dark circle is the mean value of $[\text{}^3\text{He}/\text{}^3\text{H}]$, derived from groundwater sampling in SPINP water intake in 1991–1992



Now we can find the concentration ratios of the daughter (${}^3\text{He}$) and parent (${}^3\text{H}$) radionuclides: $\overline{C}_{21} = 1.1$. In farther analysis, we use the solution (3.47), assuming $t_{\text{calc}} = 40$ yrs (1992 minus 1952, i.e., the time that have passed since the beginning of global discharges of tritium into the atmosphere, see Sect. 3.4.2.1). The plot (Fig. 3.14) in coordinates $\overline{C}_{21} - \varepsilon^*$, gives the projection of the intersection point of the horizontal line $y = 1.1$ with the curve $\overline{C}_{21} \equiv [{}^3\text{He}/{}^3\text{H}]$, yielding the required value $\varepsilon^* = 0.12 \text{ year}^{-1}$.

With the mean infiltration rate of $4 \cdot 10^{-4} \text{ m day}^{-1}$ ($= 146 \text{ mm yr}^{-1}$) and the mean thickness of the aquifer of $m = 60 \text{ m}$, we have $\phi = 0.02$ (2%), which is in general agreement with the current concept of fracture porosity of karstified rocks. Data treatment with no allowance made for the character of input function yields far overestimated values of ϕ (by about 10%). Estimating the turn-over time τ_0 by using the reciprocal to ε^* , we obtain about 8 years.

3.4.4 Hydrodynamic Interpretation of Groundwater Isotopic Data from a Site of Deep Liquid Radioactive Waste Disposal, Siberia Chemical Combine, Russian Federation

3.4.4.1 Background Information About the Radioactive Waste Disposal Site

The site is located in the southern West-Siberian Plain on the right bank of the Tom River, 15 km north of Tomsk City (Fig. 3.15). Geologically, the area belongs to the northwestern limb of Tomsk sinclinorium. The geologic section (Fig. 3.16) has a two-stage structure (Rybalchenko et al. 1998; Zubkov et al. 2005):

- lower structural stage – complexly folded, metamorphized terrigenous rocks of coastal-marine facies, Devonian-Carboniferous (Paleozoic);

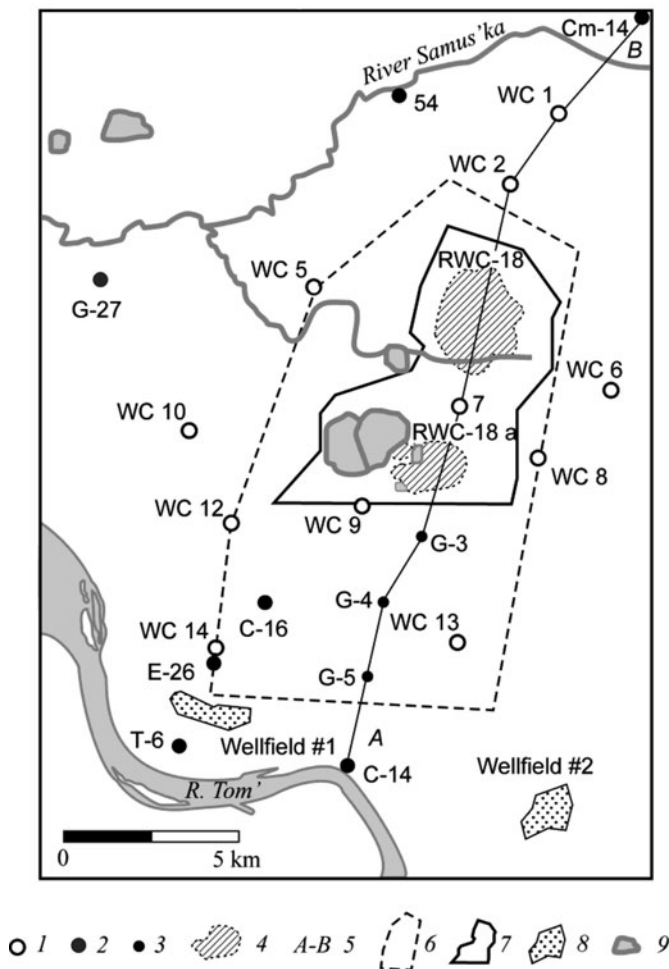


Fig. 3.15 Layout of sampling area. (1) Cluster of observation wells, (2) single well, (3) geological well, (4) area affected by radionuclide contamination, (5) section line; boundaries of (6) mining allotment and (7) restricted zone of the RW disposal site; (8) water supply system; (9) surface water reservoir

- upper structural stage – terrigenous, mostly continental, poorly consolidated deposits of platformal mantle of Cretaceous, Paleogene, Neogene, and Quaternary (Meso-Cenozoic).

The sand-clay Meso-Cenozoic strata comprises (Rybalchenko et al. 1998; Pozdniakov et al. 2005): a complex of Cretaceous deposits represented by (I–IV) sand and (A, B, C, D) clay horizons, and a complex of Paleogene and Quaternary deposits in (IV, IVa, V, VI) sand and (E, F, G) clay (semipervious beds). In terms of hydrogeological stratification, two aquifer systems can be identified in the section:

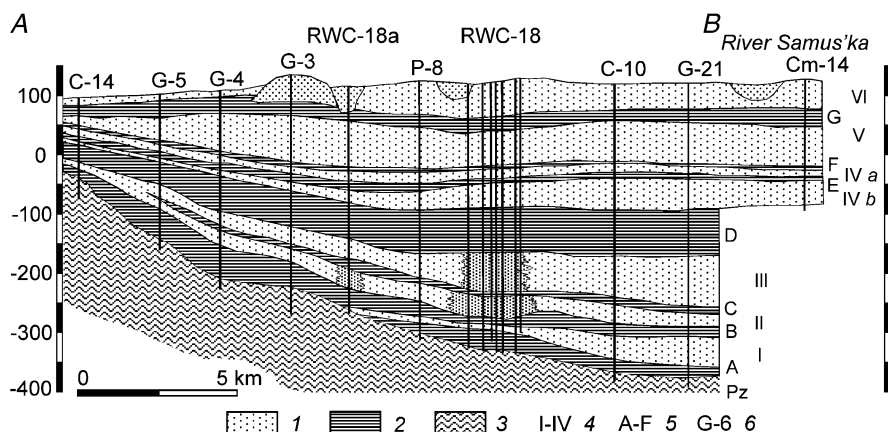


Fig. 3.16 Geological section. (1) Aquifers (mostly sand parts of the sedimentary section); (2) aquitards (beds with clay predominance in the sedimentary section); (3) metamorphic rocks of Paleozoic basement; (4) aquifer numbers (II and III are reservoir beds, I and IV are semipervious horizons); (5) separating layers; (6) well numbers. The dashed zone near wells in areas 18 and 18a is the spreading zone of radioactive solutions

the lower (aquifers I–III) and the upper (aquifers IV, IVa, V, and VI); the systems are separated by a low-permeability (clay) bed (aquitard) D. The total transmissivity reaches $1,600 \text{ m}^2/\text{day}$ in aquifers IV–VI and $60\text{--}80 \text{ m}^2/\text{day}$ in aquifers I–III (with hydraulic conductivity of $0.5\text{--}2 \text{ m/day}$ (Shestakov et al. 2002)). The hydraulic conductivity of the separating (clay) beds is of the order of $10^{-2}\text{--}10^{-4} \text{ m/day}$ (for bed D, $k \approx 1 \cdot 10^{-4} \text{ m/day}$). Groundwater of the lower aquifer system is hydrocarbonate calcium with mean TDS of 0.3 g/l .

The water-bearing strata are mostly recharged by infiltrating precipitation (with a mean rate of 48 mm/year , including evapotranspiration (Shestakov et al. 2002)). Groundwater flow discharges into river network and accounts for as large as 80% of infiltration recharge volume (Shestakov et al. 2002). Supposedly, the zone of water resources formation is bounded from the northeast by a subsurface water divide coinciding with the surface water divide of the Tom and Chulym rivers (about $25\text{--}30 \text{ km}$ from the RW disposal site).

Liquid radioactive waste (RW) is being disposed in the Upper Cretaceous aquifers (II and III), composed mostly of sands with varying grain size, separated from the overlying and underlying aquifers mostly by clay impermeable beds (Fig. 3.16). The first portions of liquid RW were pumped into the aquifers in 1963. The volume of pumped solution is in excess of 43.5 million m^3 . The total activity exceeded $1,000 \text{ million Ci}$. Two recharge well clusters (RWCs) with conventional numbers of 18 and 18a (Figs. 3.15 and 3.16) are operated in the site; these waste disposal sub-systems include also monitoring wells (see a detailed map in Fig. 25.1).

The liquid RW, belonging to the class of low-level radioactive waste (LLW), are being injected through wells penetrating aquifers II and III within RWC-18. The total volume of LLW buried in these collector beds is about 40 million m³. The total salt content of radioactive solutions never exceeds 20 g/l, and their activity varies from 10⁻⁸ to 10⁻⁶ Ci/l. Intermediate-level radioactive waste (ILW) are injected through wells into aquifer II within RWC-18 a with much lower rate. These are brines with the total salt content of up to 300 g/l and the activity of up to N·10⁻² Ci/l. The decay of short-lived radioactive elements in the composition of ILW causes rock warming to the temperature far in excess of water boiling point (up to 170°C). The migration of radioactive solutions is accompanied by various physicochemical processes discussed in Sect. 23.1 and Chap. 25.

The upper aquifers (V and VI) are tapped by two wellfields, located 10 and 13 km south of the disposal site. In this case, in addition to the studies of the safety of RW underground disposal (Rybalchenko et al. 1998), of some interest can be the direct assessment of hydrodynamic characteristics that determine the risk of water use.

In this context, this section is devoted to the analysis of the intensity of *regional groundwater flows* based on isotopic data collected from samples taken in monitoring network in 2003–2004.

3.4.4.2 Field Data

Water samples were taken from wells of the monitoring network (Tokarev et al. 2005; Tokarev et al. 2009a, b), equipped with hole filters in five major horizons (Fig. 3.15): reservoir beds (host aquifers) II, III used for RW disposal; aquifers I and IV are located below and above the reservoir beds; and a water-producing aquifer V. One sample was taken from well C-115, tapping the rocks of Paleozoic basement (hereafter denoted by index F), underlying I aquifer.

The taken samples were analyzed to determine ⁴⁰Ar concentration by volumetric method and the isotopic ratios ⁴⁰Ar/³⁶Ar, ²⁰Ne/⁴He and ³He/⁴He by mass-spectrometric method. ⁴He isotope concentrations, [⁴He], were calculated by using [²⁰Ne/⁴He]_{obs} isotopic ratio, measured by a mass spectrometer. Since the only source of ²⁰Ne in groundwater can be atmospheric air, its concentration, [²⁰Ne]_{atm}, in groundwater of infiltration genesis is determined by the degree of water saturation by this gas in the moment of precipitation infiltration. The formula for calculation can be written as

$$[{}^4\text{He}] \equiv C_2 = [{}^{20}\text{Ne}]_{\text{atm}} / [{}^{20}\text{Ne}/{}^4\text{He}]_{\text{obs}} - [{}^4\text{He}]_{\text{atm}}. \quad (3.71)$$

The amounts of atmospheric gases ²⁰Ne_{atm} and ⁴He_{atm} can be calculated given the temperature at which water was in contact with the atmosphere. This temperature was derived from the measured argon concentrations in water samples by the conventional procedure (Weiss 1971; Mazor 1972). Table 3.2 gives estimated water temperature in the zone of influence of the disposal ground (RWC-18).

Table 3.2 Temperature of argon dissolution in water, °C

Aquifer	Region	WRC-18
II	+1.4(8) ^a	+16.8(6)
III	−0.2(8)	+12.4(4)
IV	+2.6(8)	+0.9(1)
V	+4.2(7)	+0.1(1)

^aThe number of analyses (given in parentheses)

Thus, given the concentrations of $^{20}\text{Ne}_{\text{atm}}$ and $^4\text{He}_{\text{atm}}$ and the ratios $[^{20}\text{Ne}/^4\text{He}]_{\text{obs}}$, the current values of $[^4\text{He}]$ concentration were evaluated by (3.71) (see Table 3.3). Table 3.3 contains wells (36 in total), lying beyond the boundaries of the zone of influence of injection wells used for radioactive waste disposal.

As one may see, the observed helium concentrations in groundwater of different aquifers cover a range of three orders of magnitude ($\approx 3 \cdot 10^{-8}$ to $1.4 \cdot 10^{-5}$ $\text{cm}^3 \text{STP g}^{-1} \text{H}_2\text{O}$). Water in the lower part of the section is enriched in ^4He . The highest concentration was recorded in the well that tapped water occurring below the first aquifer ($[^4\text{He}] = 1.37 \cdot 10^{-5}$ $\text{cm}^3 \text{STP g}^{-1} \text{H}_2\text{O}$). The average concentration of ^4He ($[^4\text{He}]_{\text{aver}}$) in reservoir beds (aquifers) I–III is of the order of $\text{N} \cdot 10^{-6}$ $\text{cm}^3 \text{STP g}^{-1} \text{H}_2\text{O}$, with statistically significant concentrations of $[^4\text{He}]$ in reservoir bed III being lower than in reservoir beds I and II. The concentration in the superior aquifer IV decreases by about an order of magnitude ($[^4\text{He}]_{\text{aver}} = 3.92 \cdot 10^{-7}$ $\text{cm}^3 \text{STP g}^{-1} \text{H}_2\text{O}$). Finally, $[^4\text{He}]_{\text{aver}}$ concentration in aquifer V is even less ($6.81 \cdot 10^{-8}$ $\text{cm}^3 \text{STP g}^{-1} \text{H}_2\text{O}$). Thus, ^4He concentration features nearly exponential decrease with increasing elevation of water-bearing rocks.

The model structure involves evaluating the production rate, P_i , of radiogenic ^4He by water-bearing rocks. Such estimates were based on data of studying the composition of rock samples taken from the key well CH-118. Analysis of uranium and thorium concentrations in rocks shows that rocks in the upper part of the section feature higher natural radioactivity (Table 3.4), while variations in their concentrations within individual lithologic members in such zones are relatively narrow.

3.4.4.3 Quantitative Interpretation of Sampling Results

The conventional approach, assuming the accumulation of ^4He exclusively due to the decay of natural radionuclides in aquifers I–V (see formula 3.70), yields obviously overstated groundwater age: many hundreds of thousands to millions of years for lower aquifers and tens to hundreds of years for upper aquifers. It is reasonable to suppose that such errors are due to the existence of an additional source of radiogenic ^4He in groundwater in deep-seated zones of Earth's crust (Martel et al. 1989; Castro et al. 2000; Kulongoski et al. 2008; see also Sect. 3.3.4.2). Thus more complete is the model that takes into account not only the production of this gas by natural radionuclides in host rocks but also its input into the stratified formation from large depths and its diffusion-based redistribution among individual aquifers.

Preliminary analysis of the hydrogeological situation and sampling data allows the regional section of the territory to be assumed to comprise the following four

Table 3.3 Estimated concentrations of radiogenic ^4He (cm³STP g⁻¹H₂O) in aquifers

Aquifer	Monitoring system	Well number	[^4He]	[^4He] _{aver}
F ^a	RNW ^c	C-115	$1.37 \cdot 10^{-5}$	$1.37 \cdot 10^{-5}$
I	RNW	G-27	$5.52 \cdot 10^{-6}$	$4.78 \cdot 10^{-6}$
	WC 5 ^b	C-6	$5.15 \cdot 10^{-6}$	
	WC 9	CH-117	$5.46 \cdot 10^{-6}$	
	WC 3	No 54	$3.00 \cdot 10^{-6}$	
II	WC 1	No 49	$4.82 \cdot 10^{-6}$	$5.28 \cdot 10^{-6}$
	WC 7	G-2	$1.76 \cdot 10^{-6}$	
	RNW	C-16	$6.34 \cdot 10^{-6}$	
	WC 2	CH-84	$4.3 \cdot 10^{-6}$	
	WC 5	CH-87	$4.12 \cdot 10^{-6}$	
	WC 12	CH-93	$7.82 \cdot 10^{-6}$	
	WC 13	CH-98	$5.33 \cdot 10^{-6}$	
	WC 10	CH-106	$7.82 \cdot 10^{-6}$	
III	WC 1	No 59	$1.76 \cdot 10^{-6}$	$3.34 \cdot 10^{-6}$
	WC 2	CH-85	$1.63 \cdot 10^{-6}$	
	WC 5	CH-86	$4.04 \cdot 10^{-6}$	
	WC 6	CH-88	$4.82 \cdot 10^{-6}$	
	WC 12	CH-94	$3.10 \cdot 10^{-6}$	
	WC 13	CH-96	$2.10 \cdot 10^{-6}$	
	WC 10	CH-110	$5.97 \cdot 10^{-6}$	
IV	WC 2	No 46	$2.28 \cdot 10^{-7}$	$3.92 \cdot 10^{-7}$
	WC 1	No 50	$9.52 \cdot 10^{-8}$	
	WC 10	CM-6	$6.69 \cdot 10^{-7}$	
	WC 7	CH-91	$3.29 \cdot 10^{-7}$	
	WC 12	CH-95	$9.02 \cdot 10^{-7}$	
	WC 13	CH-97	$6.51 \cdot 10^{-7}$	
	WC 6	CH-102	$1.15 \cdot 10^{-7}$	
	WC 5	CH-104	$1.46 \cdot 10^{-7}$	
V	RNW	E-26	$1.17 \cdot 10^{-7}$	$6.81 \cdot 10^{-8}$
	RNW	T-6	$5.04 \cdot 10^{-8}$	
	WC 9	CH-100	$5.54 \cdot 10^{-8}$	
	WC 2	No 47	$4.69 \cdot 10^{-8}$	
	WC 1	No 51	$3.03 \cdot 10^{-8}$	
	WC 6	CH-103	$9.18 \cdot 10^{-8}$	
	WC 5	CH-105	$5.28 \cdot 10^{-8}$	
	WC 10	CH-114	$1.00 \cdot 10^{-7}$	

^aF is Paleozoic foundation^bWC is the cluster of observation wells penetrating different aquifers (Waste Disposal site's monitoring system)^cRNW is regional observation well network

basic (model) beds (Table 3.5) (from bottom to top): the first, combining aquifers I and II; the second bed is aquifer III; the third bed is aquifer IV; and the fourth bed is aquifer V. The sources of ^4He are radioactive decay of elements of uranium–thorium

Table 3.4 Concentrations of natural radionuclides in the upper and lower parts of the geological section (in g/g)

Aquifer	Uranium-238 $C_1^{1,W} \cdot 10^6$	Thorium-232 $C_1^{3,W} \cdot 10^6$
IV and V	2.27	7.42
II and III	1.26	5.34
Average	1.77	6.38

Table 3.5 Input data for calculating horizontal fluxes with groundwater in the stratified formation based on ^4He method

Index	Parameters of the system				
i	Aquifers and semipervious beds	$m_i, m_{0i}(\text{m})$	$m_{vi}^c(\text{m})$	$[^4\text{He}]_i^d \left(\frac{\text{cm}^3\text{STP}}{\text{gH}_2\text{O}} \right)$	$\alpha_i \left(\frac{1}{\text{yr}} \right) \quad P \left(\frac{\text{cm}^3\text{STP}}{\text{gH}_2\text{Oyr}} \right)$
	VI ^a	20			
	G ^b	15	55	$6.8 \cdot 10^{-8}$	$1.9 \cdot 10^{-5}$
4	V	55			
	F	10			$4.2 \cdot 10^{-5} \quad 3.6 \cdot 10^{-12}$
3	IVa, IV (E)	75(85) ^c	65	$3.9 \cdot 10^{-7}$	
	D	40 (60)			$2.0 \cdot 10^{-5}$
2	III	40 (60)	35	$3.3 \cdot 10^{-6}$	
	C	15 (20)			$3.8 \cdot 10^{-5} \quad 2.3 \cdot 10^{-12}$
1	I, II (B)	55 (90)	40	$(4.8 - 5.3) \cdot 10^{-6}$	

^aThe numbers (roman numerals) of aquifers^bIndices (roman letters) of semipervious beds^cThe total thickness of the flow-carrying zones within the i th model bed^dThe mean value (see Table 3.3)^eThe values (figures in parentheses) corresponding to the mean bed thicknesses near the RWCs

series and the regional flux of this gas from the foundation. The system is open with respect to the topmost (VI) aquifer, where ^4He concentration was assumed zero.

In accordance with this model, the process is described by the system of differential Eqs. 3.68, such that the governing parameters are (Table 3.5): the thickness of pervious and semipervious (separating) beds, m_i and m_{0i} , their porosity, ϕ_i , specific discharge, q_i , the rate of ^4He production due to the decay of natural radionuclides, P_i , interlayer exchange coefficients, α_i , abyssal helium flux, J_0 ; $i = 1, 2, 3, 4$.

The characteristics assumed to be constant in the interpretation of isotopic data are taken to be bed thicknesses (the “regional” values somewhat differ from those within the disposal site (Table 3.5)); porosity (the mean over all beds is $\phi \equiv \phi_i = 0.25$); ^4He production rate ($P_1 = P_2, P_3 = P_4$); interlayer diffusion exchange coefficients, α_i . The latter were calculated by (3.68a), where helium molecular diffusion coefficient, D_e , was derived from the relationship $D_e/\phi = 3.46 \cdot 10^{-4} \text{ m}^2/\text{d}$ ($4.0 \cdot 10^{-9} \text{ m}^2/\text{s}$) (Castro et al. 2000), whence with $\phi = 0.25$ we have $D_e = 0.0315 \text{ m}^2/\text{yr}$. The high value of D_e is due to the high mobility of this isotope in the subsurface

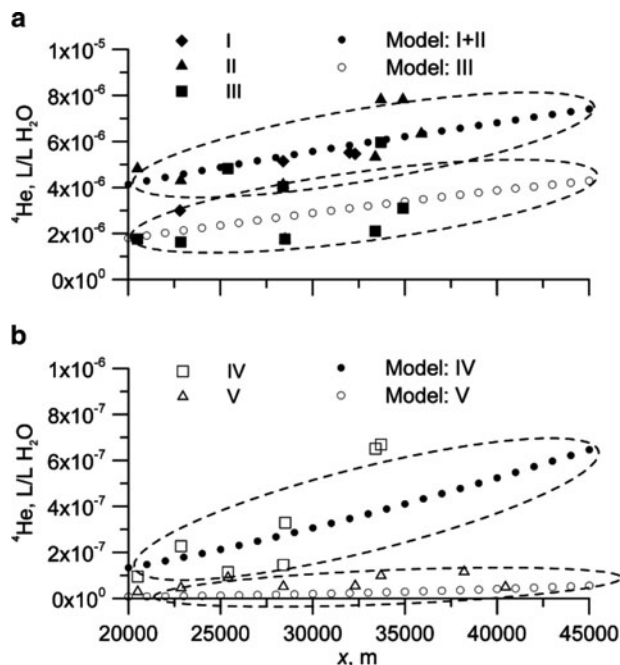


Fig. 3.17 Actual and model ^4He concentration distributions in (a) I–III and (b) IV–V aquifers

hydrosphere, which is greater than the respective characteristics for components, such as Cl^- and ^3H (Sato et al. 2001). The value of P_i (Table 3.5) was estimated by (3.70d) with data of Table 3.4 and $\rho_b = 2.5 \text{ g cm}^{-3}$.

The parameters being fitted were Darcy velocity, q_i , and the regional vertical helium flux, J_0 . The goal functions were ^4He concentration distributions $C_i = f(x)$ in the appropriate (i th) beds (Fig. 3.17). The coordinate x was measured along flow lines from the water-divide line between the Tom and Chulym river valleys. In accordance with regional modeling data (Shestakov et al. 2002), these are the areas where the aquifers receive the major portion of their infiltration recharge. Notwithstanding the approximate character of such approach to determining the layout of concentration measurement points, the obtained plots (Fig. 3.17) unambiguously demonstrate a tendency toward the accumulation of radiogenic ^4He (an increase in the current concentration) during the flow of groundwater from the recharge to the discharge area.

The parameters listed above were fitted by multivariant solution of the system of differential Eqs. 3.68. The result was the choice of a single solution best describing the spatial distribution of ^4He in all aquifers (Fig. 3.17). This solution corresponds to the values of specific discharge given in Table 3.6 and the mass flux of abyssal helium $J_0 \approx 1 \cdot 10^{-8} \text{ cm}^3 \text{ STP cm}^{-2} \text{ yr}^{-1}$.

The obtained values of q_i are in general agreement with earlier hydrodynamic estimates (Table 3.6). The largest deviations were recorded with data given in

Table 3.6 Comparison of estimated mean specific discharge values q_i (m yr^{-1}) in aquifers, obtained with the use of ^4He isotope distributions in the aquifer system

Aquifer	^4He method	Rybalchenko et al. 1998	Shestakov et al. 2002
V	5.0	–	7.3
IV	2.0 (2.6) ^a	–	2.6
III	0.5	0.75–1.25	0.26
I + II	0.6 (0.83)		

^aThe Darcy velocities (figures in parentheses in the second column are the) estimated based on the effective thickness of the flow, m_v (see Table 3.5)

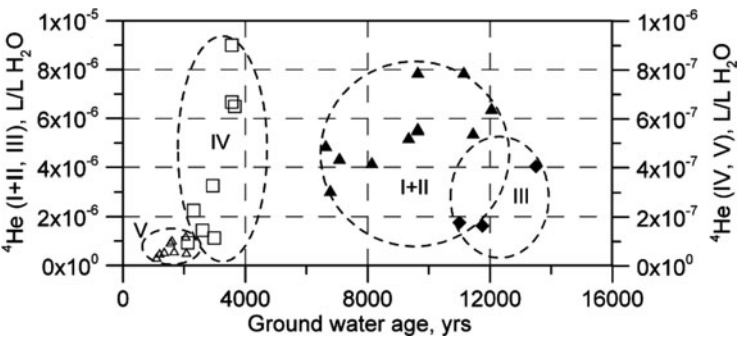


Fig. 3.18 Water age in different aquifers estimated by uranium–helium method. The legend see in Fig. 3.17

(Shestakov et al. 2002) for lower aquifers I–III: the specific discharge derived from the interpretation of helium sampling results is about twice as large as the values obtained from the solution of regional groundwater flow problem.

Finally, based on the obtained values of q_i , we can assess groundwater age in all sampling points, x : $t_{0i} = x\phi/q_i$ (Fig. 3.18). Water age varies from 7 to 14 thousand years (with a mean of about 9 thousand years) in the lower aquifers (I–III), from 2 to 4 thousand years in aquifer IV, and from 1 to 2 thousand years in the upper aquifer V.

The obtained values of groundwater age characterize the migration intensity of chemically inert particles (in this case, components that are not adsorbed by rock). The velocity of radionuclides becomes much slower because of adsorption on aquifer solids and co-precipitation with mineral salts, which precipitate during the interaction between radioactive solutions and formation waters on moving geochemical barriers (Rumynin et al. 2005a, b; see also Sect. 23.1). The sorption retention factor is estimated at tens (for decay products, such as ^{90}Sr and ^{137}Cs) and hundreds relative units (for actinides, such as ^{239}Pu , ^{241}Am , etc.). This means that the radionuclide residence times in reservoir beds should be at least hundreds of thousand years, a period which is quite sufficient for the self-purification

of radioactive wastes due to radioactive decay (in combination with adsorption). This conclusion confirms once again the safety of the scheme of liquid RW disposal by their injection into deep aquifers chosen at this plant.

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Chapter 4

Profile (Two-Dimensional in Vertical Cross-Section) Models for Solute Transport in Regional Flow Systems

Vertical concentration gradients in natural systems can be rather large, often created by contaminant release near the water table as occurs in case of non-point contamination sources formed under the areal recharge conditions. Therefore the regional horizontal flow models discussed in the previous chapter have some serious limitations: neglecting the real redistribution of pollutants over the aquifer depth, such models allow one to calculate only vertically averaged concentration profiles. For example, such formulation of the problem is too coarse when migration processes are studied on the basis of hydrogeological monitoring data from wells penetrating thick (tens of meters) water-bearing strata. The propagation velocities of concentration fronts in individual profile zones can also differ from the averaged estimates. The prerequisites for the formation of contrast hydrogeochemical zonality are (a) the infiltration character of phreatic-water pollution and (b) the nonuniform distribution of rock permeability.

4.1 Problem Statement

The area distribution of groundwater recharge is among the factors governing the two-dimensional (in the vertical plane) character of groundwater flow velocity field. Apart from the horizontal component, which accounts for the major portion of groundwater flow discharge along the bedding and determines the rate of subhorizontal mass transport, there exists a vertical component of flow velocity, contributing to the gradual sinking of polluted water from the roof of the bed toward deeper zones near its foot. Since the intensity of vertical advection is usually small, the lower parts of the section can remain “clear” for a long time, whereas the real concentrations in the upper zones will be many times as large as the values calculated before for two-dimensional horizontal flows (Robertson and Cherry 1989; Robbins 1989). The focusing of solutes, delivered by infiltration water, in the upper part of the section is supported by a vast body of data from isotopic sampling of aquifers. Infiltration also contributes to the dilution of polluting solutions beyond the boundaries of the surface pollution source.

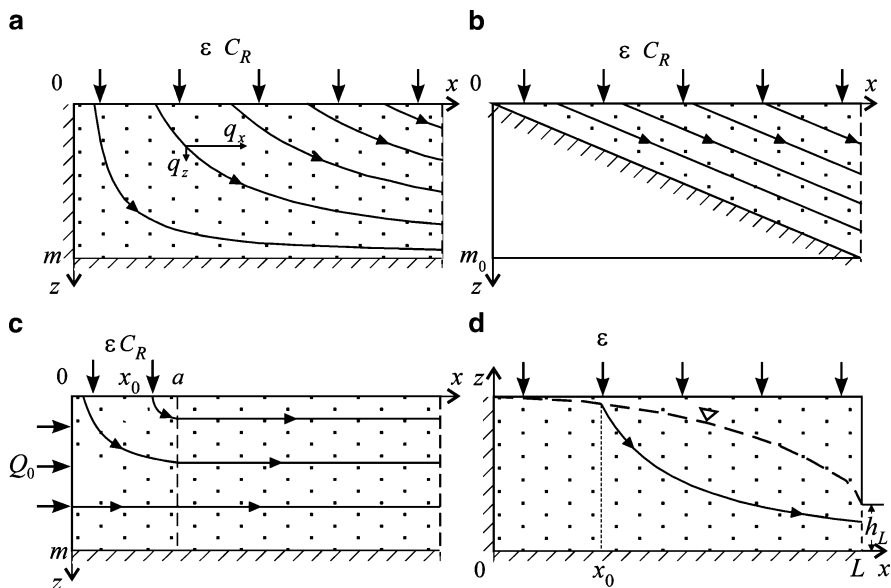


Fig. 4.1 Geometry and boundary conditions for idealized groundwater flow profiles. (a, b) Confined aquifers with constant and linearly increasing thickness with uniform infiltration recharge, respectively; (c) a confined aquifer with concentrated infiltration, (d) an unconfined aquifer

The stratification of the section causes additional differentiation of solute in the flow profile. Thus, solute transport takes place mostly through high-permeability zones. However, the migration through such prevailing paths is hampered by molecular diffusion outflux of solute into low-permeability parts of the section; in stratified systems, advective exchange between layers also should be taken into account (Chap. 5).

In our study, the flow pattern can be schematized as a quasi-2D (in cross-section) unilateral (unidirectional in plane view) flow towards a perfect outlet boundary (a drain), ignoring a transverse flow component in the vicinity of it (Fig. 4.1). In hydrogeological analysis, such flow pattern can be associated with a flow in a semi-infinite aquifer or with a fragment of a profile flow path within a groundwater catchment. Thus, the configuration of the flow problem corresponds to the typical case known as “well-mixed reservoir” that generates an exponential-like transit time distribution at the outlet (Cornaton and Perrochet 2006; see also Sect. 3.1.3).

If the aquifer is homogeneous and *confined* and is uniformly recharged on top by a constant-rate infiltration (Fig. 4.1a), then the following expressions can be written for flow velocity potential, φ , and stream function, ψ (Polubarinova-Kochina 1962; see also Sect. 1.2.2):

$$\varphi = -\frac{\varepsilon}{2m}[x^2 - (z-m)^2] + \varphi_0, \psi = -\frac{\varepsilon}{m}x(z-m) + \psi_0, \quad (4.1)$$

where ε is the areal recharge rate [LT^{-1}], m is the aquifer thickness; φ_0 and ψ_0 are integration constants [L^2T^{-1}]. From the no-flow condition on the lower boundary of the bed ($z = m$ $\psi = 0$), we obtain $\psi_0 = 0$, resulting in $\psi = \varepsilon x(1 - z/m)$.

Thus, the groundwater flow in homogeneous rock formations can be described by functions φ and ψ , belonging to the family of focused hyperbolas. Equation 4.1 satisfy the Cauchy–Riemann Eq. 1.63 for the profile problem, $y \equiv z$, whence, in particular, it follows: $q_x = -\partial\varphi/\partial x = \varepsilon x/m$ and $q_z = \partial\psi/\partial x = \varepsilon(1 - z/m)$ – the horizontal and vertical components of Darcy velocity [LT^{-1}]. In the case of *unconfined flow* or heterogeneous beds, as can be discussed below, the expressions for functions φ and ψ radically change (Bear 1972).

Therefore, when searching for analytical expressions for particle motion trajectories in the bed profile, one may need to determine the basic components of groundwater flow velocity from other solutions of hydrodynamic problems (Polubarinova-Kochina 1962; Shestakov 1995). Such analysis most often begins with the consideration of the *continuity equation* for homogenous fluid flow:

$$\frac{\partial q_x}{\partial x} + \frac{\partial q_z}{\partial z} = 0. \quad (4.2)$$

To describe the spatial and temporal characteristics of flow and to find the trajectories of water particles, the system of first-order ordinary differential Eq. 1.32a, can be considered (for 2D profile $u_y(q_y) = 0$). If a particular parameterization t of the characteristic curves is fixed, then these equations may be written as a system of ordinary differential equations for $x(t)$, $z(t)$:

$$\begin{aligned} \frac{dx}{dt} &= \frac{q_x}{\phi}, \\ \frac{dz}{dt} &= \frac{q_z}{\phi}; \end{aligned} \quad (4.3)$$

this system is also referred to as system of *characteristic equations*.

Now let us discuss how such problem formulation can be applied to studying migration processes taking place under different hydrogeological conditions.

4.2 Homogeneous Confined Aquifer

4.2.1 Flow Velocity Field

Suppose that *Dupuit–Forchheimer assumption* is among the conditions of the problem, meaning that the horizontal hydraulic gradients do not change over depth z in any vertical section of the flow x . Now, in a homogeneous, semibounded, *constant-thickness confined* aquifer (Fig. 4.1a), the horizontal flow velocity (see formula (3.1a) with $q_0 = 0$) becomes

$$q_x = \varepsilon \bar{x}, \quad \bar{x} = x/m. \quad (4.4)$$

Integrating the expression (4.2)

$$\frac{\partial}{\partial x} \int_0^z q_x dz - q_x|_{z=z} \frac{\partial z}{\partial x} + q_z|_{z=z} - q_z|_{z=0} = 0 \quad (4.4a)$$

with the assumption that $q_z = \varepsilon$ at the upper boundary ($z = 0$) of the flow, we obtain

$$q_z = \varepsilon(1 - \bar{z}), \quad \bar{z} = z/m. \quad (4.4b)$$

The application of formulas (4.4) and (4.4b) under real conditions implies the assumption that the deformation of groundwater flow net is only slightly deformed under the effect of the outlet boundary (Haitjema 1995). However for a hydrogeological system with a small spacing relative to the aquifer thickness, the Dupuit–Forchheimer assumption may not hold (Groenendijk and van den Eertwegh 2004).

For a *confined aquifer with linearly increasing thickness* and uniform recharge (Fig. 4.1b), the Darcy velocity is constant (does not depend on space coordinates)

$$q_x = \varepsilon/\gamma, \quad q_z = \varepsilon, \quad (4.4c)$$

where $\gamma = \Delta z/\Delta x$ is bed foot slope.

The *unconfined* character of groundwater flow (Fig. 4.1d), increasing the complexity of the profile structure of the flow, affects the groundwater flow field as well. The continuity equation of flow in a profile Dupuit–Forchheimer model is

$$\frac{\partial Q_x}{\partial x} = \frac{\partial}{\partial x}(hq_x) = \varepsilon, \text{ or } q_x \frac{\partial h}{\partial x} + h \frac{\partial q_x}{\partial x} = \varepsilon, \quad (4.5)$$

where $h \equiv h(x)$ is the saturated aquifer thickness. Using the continuity Eq. 4.2 gives for the derivative q_z

$$\frac{\partial q_z}{\partial z} = \frac{1}{h} \left(q_x \frac{\partial h}{\partial x} - \varepsilon \right), \quad (4.5a)$$

which, integrated over the saturated aquifer thickness, results in the following expression for q_z (Polubarinova-Kochina 1962; Strack 1989):

$$q_z = \frac{z}{h} \left(q_x \frac{\partial h}{\partial x} - \varepsilon \right); \quad (4.5b)$$

z -axis is directed vertically upward (as in Fig. 4.1d), therefore, unlike (4.4b), $q_z < 0$. The first term in parentheses in (4.5b) is due to the curving phreatic surface (Haitjema 1995).

The relationships for horizontal and vertical components of groundwater flow velocity can be represented in another form

$$q_x = -k \frac{dh}{dx}, \quad q_z = -\frac{dq_x}{dx} z = k \frac{d^2 h}{dx^2} z, \quad (4.5c)$$

where k is hydraulic conductivity. For the flow pattern in Fig. 4.1d (Polubarinova-Kochina 1962; Bear 1972; Shestakov 1995), we have:

$$h(x) = \sqrt{\frac{\varepsilon}{k}(L^2 - x^2) + h_L^2}, \quad (4.5d)$$

where L is the distance from the water divide to the perfect hydrodynamic boundary of the first type (river or lake), where the head is h_L .

In general, the 2D profile flow models based on the Dupuit–Forchheimer assumption provide the simplest basis for estimating flow path pattern and travel times, as well as for concentration field description.

4.2.2 Flow Kinematic Equations and Concentration Distributions

4.2.2.1 Space-Time Characteristics

The substitution of Eqs. 4.4 and 4.4b into system of Eq. 4.3 allows us to separate variables and rewrite this system in the integral form:

$$\int_{\bar{x}_0}^{\bar{x}} \frac{d\bar{x}}{\bar{x}} = \int_0^{\bar{z}} \frac{d\bar{z}}{1 - \bar{z}} = \frac{\varepsilon}{m\phi} \int_0^t dt \quad (4.6)$$

(groundwater flow in a *constant-thickness* aquifer, Fig. 4.1a). Whence we easily find the current (at time t) coordinate of any particle (x, z), arriving on the bed surface $z = 0$ in point $x = x_0$ (the distance between infiltration point and groundwater divide) at moment $t = 0$:

$$\bar{x} = \bar{x}_0 e^{\varepsilon^* t}, \quad \bar{z} = 1 - e^{-\varepsilon^* t}, \quad \varepsilon^* = \varepsilon/m\phi, \quad (4.7)$$

i.e., the streamline equation

$$\bar{x}(1 - \bar{z}) = \bar{x}_0. \quad (4.7a)$$

When the solute is uniformly supplied onto the entire watershed surface, it will appear at the same depth z from the surface in the moment

$$t = \frac{1}{\varepsilon^*} \ln(1 - \bar{z})^{-1} \quad (4.7b)$$

in any section x (Vogel 1967; Hoeks 1981). Thus, contours of travel time which can be associated with the groundwater age are horizontal lines, because the vertical velocity does not depend on the horizontal scale (see Eq. 4.4b). An important consequence of the age distribution in this system is that large differences in age can occur over relatively short vertical distances when the recharge rate is small (Solomon et al. 2006).

On the other hand, substituting the value of $\bar{z}$ from the equation for an arbitrary flow line into the latter expression, we find the migration time of the particle in the interval $[x_0, x]$:

$$t_0 \equiv t_0(x) = \frac{1}{\varepsilon^*} \ln \left(\frac{\bar{x}}{\bar{x}_0} \right). \quad (4.7c)$$

A similar approach to mathematical formulation of regional flow under areal recharge conditions can be used to solving radial solute transport problems (Hoeks 1981). Thus, in *convergent radial flow* the transport time, t_0 , between infiltration point, x_0 , and a discharge well can be found using following equation:

$$t_0 \equiv t_0(x=r) = \frac{1}{\varepsilon^*} \ln \left[1 - \left(\frac{r-x_0}{r} \right)^2 \right], \quad (4.7d)$$

where r is the distance between the well and groundwater divide.

For a confined aquifer with *linearly increasing thickness* and uniform recharge (Fig. 4.1b)

$$x = x_0 + z/\gamma, \quad t = z\phi/\varepsilon, \quad (4.7e)$$

i.e., x and t are linear functions of z . Flow lines are parallel to the aquifer foot (Fig. 4.1b), and the travel time is independent of the horizontal location of the aquifer.

In the *unconfined* formulation of problem (Fig. 4.1d), the integration of the first equation of the system (4.3), where q_x is determined by (4.5c)–(4.5d), yields

$$t_0 = \frac{\phi}{\varepsilon} \int_{x_0}^x \frac{\sqrt{\varepsilon(L^2 - \xi^2)/k + h_L^2}}{\xi} d\xi = \frac{\phi}{\sqrt{\varepsilon k}} \int_{x_0}^x \sqrt{\left(\frac{\alpha}{\xi^2} - 1 \right)} d\xi, \\ \alpha = L^2 + kh_L^2/\varepsilon. \quad (4.8)$$

With the introduction of the new variable $\gamma = \sqrt{\alpha/x}$ (Chesnaux et al. 2005), (4.8) becomes

$$t_0 = -\phi \sqrt{\frac{\alpha}{\varepsilon k}} \int_{\sqrt{\alpha/x_0}}^{\sqrt{\alpha/x}} \frac{\sqrt{\gamma^2 - 1}}{\gamma^2} d\gamma. \quad (4.8a)$$

Equation 4.8a can be integrated by parts. Finally Chesnaux et al. (2005) found:

$$t_0 = \phi \sqrt{\frac{\alpha}{\varepsilon k}} \left[\left(\frac{\sqrt{\beta^2 - 1}}{\beta} - \frac{\sqrt{\beta_0^2 - 1}}{\beta_0} \right) + \ln \frac{\beta_0 + \sqrt{\beta_0^2 - 1}}{\beta + \sqrt{\beta^2 - 1}} \right], \\ \beta = \frac{\sqrt{\alpha}}{x}, \beta_0 = \frac{\sqrt{\alpha}}{x_0}. \quad (4.8b)$$

We return to the confined formulation of the problem and consider the case corresponding to groundwater pollution from a source concentrated in a limited area (Fig. 4.1c), when infiltration beyond its boundary (in the domain $x > a$) can be neglected; in the calculation scheme, we also take into account the effect of natural (background) flow with a specific rate Q_0 . From the solution of the flow problem, we find the velocity field q_{xi} and q_{zi} in the first ($j = 1, 0 \leq x \leq a$) and second ($j = 2, a < x < L$) zones of the flow:

$$\begin{aligned} q_{x1} &= Q_0/m + \varepsilon \bar{x}, \quad q_{x2} = Q_0/m + \varepsilon \bar{a} \quad (\bar{x} = x/m, \bar{a} = a/m), \\ q_{z1} &= \varepsilon (1 - \bar{z}), \quad q_{z2} = 0 \quad (\bar{z} = z/m). \end{aligned} \quad (4.9)$$

The system of kinematic differential equations describing the motion of tagged particles in the first zone has the form

$$\begin{aligned} m\phi \frac{d\bar{x}}{dt} &= \frac{Q_0}{m} + \varepsilon \bar{x}, \\ m\phi \frac{d\bar{z}}{dt} &= \varepsilon (1 - \bar{z}). \end{aligned} \quad (4.10)$$

The integration of these equations over the domain $[0, t]$, $[\bar{x}_0, \bar{x}]$, $[0, \bar{z}]$ yields

$$\bar{x} = (\bar{x}_0 + \gamma) e^{-\varepsilon^* t} - \gamma, \quad \gamma = Q_0/\varepsilon a, \quad \bar{x} = x/a, \quad \bar{z} = 1 - e^{-\varepsilon^* t}. \quad (4.10a)$$

Now an arbitrary flow line originating from point $(\bar{x}_0, 0)$ can be described by the equation

$$\bar{z} = \frac{\bar{x} - \bar{x}_0}{\bar{x} + \gamma}. \quad (4.10b)$$

In the second zone, particles move parallel to x -axis along lines $\bar{z} = \bar{z}|_{\bar{x}=1}$. From these relationships it follows that the maximal penetration depth of polluted water is determined in this case by the relationship between Q_0 and the total recharge due to localized infiltration εa .

4.2.2.2 Correspondence with a Reservoir Model

In the confined formulation, the mean concentration of the tracer (in the interval $[0, m]$) is determined by the expression

$$\begin{aligned} C_{\text{aver}} \equiv C &= \frac{C_R \cdot z(t) + 0 \cdot (m - z(t))}{m} = C_R \bar{z}(t) \\ &= C_R \left(1 - \exp\left(-\frac{t}{\tau_0}\right) \right), \quad \tau_0 = \frac{1}{\varepsilon^*} \end{aligned} \quad (4.11)$$

(zero initial conditions), which can be seen to exactly correspond to the solution (3.11), obtained for the two-dimensional horizontal flow – exponential model

(see Sect. 3.1.3); here C_R is solute concentration in infiltrating water. The use of this and other similar solutions expressed in terms of mean concentration implies that significant mixing occurs in the aquifer, e.g., in long screens in water supply wells or in springs within a local discharge area.

When the solute is subject to decay, its concentration at depth z will be described by the expression

$$C(\bar{z}) = C_R \exp(-\lambda z) = C_R \exp\left[-\frac{\lambda}{\varepsilon^*} \ln(1 - \bar{z})^{-1}\right] = C_R(1 - \bar{z})^{\lambda_\varepsilon}, \quad (4.12)$$

where $\lambda_\varepsilon = \lambda m \phi / \varepsilon$. Thus, $C(\bar{z})$ is an exponential function, whose form remains the same for all sections $x = x_i$.

To find the average concentration $C_{\text{aver}} = \left(\int_0^{\bar{z}} C(\xi) d\xi + 0 \cdot (m - z) \right) / m$ (z is the position of the displacement front) in the interval $[0, m]$, we integrate (4.12):

$$C_{\text{aver}} \equiv C = C_R \int_0^{\bar{z}} (1 - \bar{\xi})^{\lambda_\varepsilon} d\bar{\xi} = \frac{C_R}{1 + \lambda_\varepsilon} \left[1 - (1 - \bar{z})^{1 + \lambda_\varepsilon} \right], \quad (4.13)$$

which, considering the second formula in (4.7) yields a solution, which can be represented in the dimensionless form

$$\bar{C} = \frac{1}{1 + \lambda \tau_0} \left[1 - \exp\left(- (1 + \lambda \tau_0) \frac{t}{\tau_0}\right) \right], \quad (4.13a)$$

where $\tau_0 = 1/\varepsilon^*$ (3.14a). Formula (4.13a) coincides with the solution (3.20)–(3.21, $t < t_0$), obtained for the two-dimensional horizontal model, while at $\lambda = 0$ (migration of a stable component) it coincides with the solution (3.11) (Gelhar and Wilson 1974). The ratio C/C_R is the ratio of solute flux through any section x to the flux of the solute entering the bed in the segment $[0, x]$. This ratio is almost insensitive to the solute's hydraulic dispersion, which takes place at the contact between infiltration and formation waters (Eldor and Dagan 1972).

Now, following transformations (3.14b) and (3.14c), we obtain a solution describing the distribution in the aquifer of an unstable solute for the case of an instantaneous (impulse) pollution of groundwater surface, through which its infiltration recharge takes place:

$$\frac{\partial \bar{C}}{\partial \bar{t}} = \frac{m \phi}{P_M} C_i = \bar{C}_i = \exp\left(- (1 + \lambda \tau_0) \frac{t}{\tau_0}\right), \quad \bar{t} = \frac{t}{\tau_0}, \quad (4.14)$$

where P_M is the density of the initial ($t = 0$) solute distribution on the surface $[\text{ML}^{-2}]$ (see 3.14b).

The mean transit time for the catchment flow path (Sect. 3.1.3) is the first normalized moment of the average arrival time of $C_i(t)$:

$$\tau_m = \frac{m_1}{m_0} = \frac{\int_0^\infty t C_i(t) dt}{\int_0^\infty C_i(t) dt} = \frac{\tau_0}{1 + \lambda \tau_0}. \quad (4.14a)$$

Thus, the mean transit time of particles leaving the catchment flow path outlet is not identical with the turn-over time (3.14a).

By analogy with (3.14d), we define the transit time distribution

$$g(t) = \frac{dF(t)}{dt} = \frac{1}{\tau_0} \exp\left(-(1 + \lambda\tau_0)\frac{t}{\tau_0}\right) = \frac{1}{\tau_0} \bar{C}_i, \quad (4.15)$$

which is a response to an instantaneous unit flux impulse over the entire catchment area; here the relative cumulative frequency distribution of transit (residence) times, $F(t)$, is determined by solution (4.13a) for dimensionless concentration. Now, the convolution integral, which allows the output function to be determined for a time-dependent boundary concentration, $C_R(t)$, takes the form

$$C(t) = \int_0^\infty g(\tau) C_R(t - \tau) e^{-\lambda\tau} d\tau, \quad (4.15a)$$

coinciding with (3.24); $g(\tau)$ is the transfer function for the stable tracer (3.14d).

Thus, average concentration functions, $C(t)$ in Eqs. 4.11/3.14, 4.13a for step-wise input signal, $C_i(t)$ in Eqs. 4.14, 3.14c for instantaneous input, and $C(t)$ in Eqs. 3.14f, 4.15a for arbitrary concentration input describe the integrated behavior of tracer transport through the catchment.

Similarly to (4.13a) and (4.14), it can be shown that the average concentrations in an aquifer with linearly increasing thickness are functions of the horizontal distance, x :

$$\bar{C} = \frac{\varepsilon}{\lambda\phi m(x)} (1 - \exp(-\lambda t)), \bar{C}_i = \frac{\phi m(x)}{P_M} C_i = \exp(-\lambda t). \quad (4.16)$$

Clearly, for such configuration of the bed, the turn-over time for the aquifer outlet boundary is $\tau_0 = m_0\phi/2\varepsilon$; this differs from the constant-thickness model (3.14 e) by the factor of 2, because the total water stored in this system is one half that stored in a system with constant thickness (Solomon et al. 2006). The age distribution, $g(t)$, is given by:

$$g(t) = \frac{dF(t)}{dt} = \frac{\varepsilon}{m_0\phi} \exp(-\lambda t), \quad (4.16a)$$

where m_0 is aquifer thickness at the outlet boundary of the flow.

4.2.3 *Semi-Analytical Solution for the Distribution of Global Tritium over the Aquifer Depth (Typical Curves)*

As before (see Sect. 3.4.2), we assume that tritium concentration in atmospheric water is a step-wise function $C_R(t^i) = C_R^i$ (see Fig. 3.9), where i is the number of the time interval ($i = 0$ corresponds to the initial moment $t = 0$). During the time

$\Delta t = t^N - t^i$ (t^N is the calculation moment), tritium decay takes place, such that its concentration at depth $\bar{z} = \bar{z}_i = 1 - e^{-\varepsilon^*(t^N - t^i)}$ in accordance with (4.8) will be

$$C \equiv C(\bar{z}) = C^0 + (C^i - C^0)e^{-\lambda(t^N - t^i)} \quad (4.17)$$

(C^0 is the background concentration).

The latter formula allows us to calculate the tritium distribution over the aquifer thickness $C = C(\bar{z})$ at fixed t^N and $\varepsilon^*(\tau_0)$. An example of such calculation is given in Fig. 4.2 (for a particular value of τ_0), where the migration of a concentration peak deeper into the aquifer can be seen well. Plots of $C(\bar{z})$ for the basic input concentration function (see Fig. 3.9) at different values of complex parameter τ_0 are given in Fig. 4.3 ($t^N = 58$ years (2010)). Their analysis shows the distributions $C(\bar{z})$

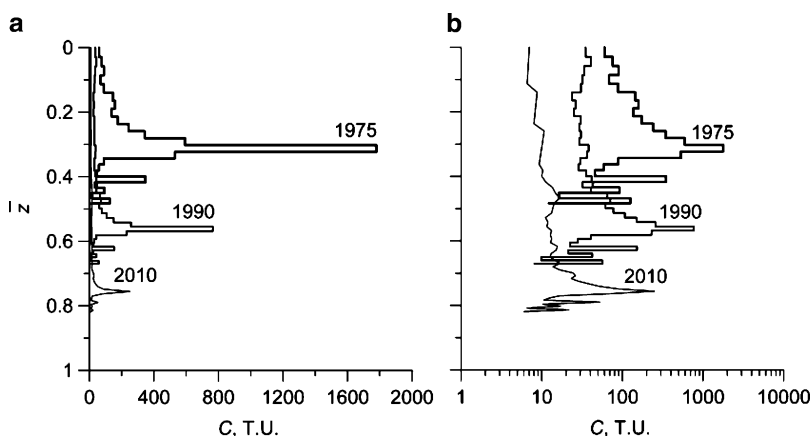


Fig. 4.2 Plots of function ${}^3\text{H}(z)$ in different moments for input concentration signal in Fig. 3.9 ($\tau_0 = 33.3$ yr). (a and b) Normal and logarithmic scales for the concentration axis

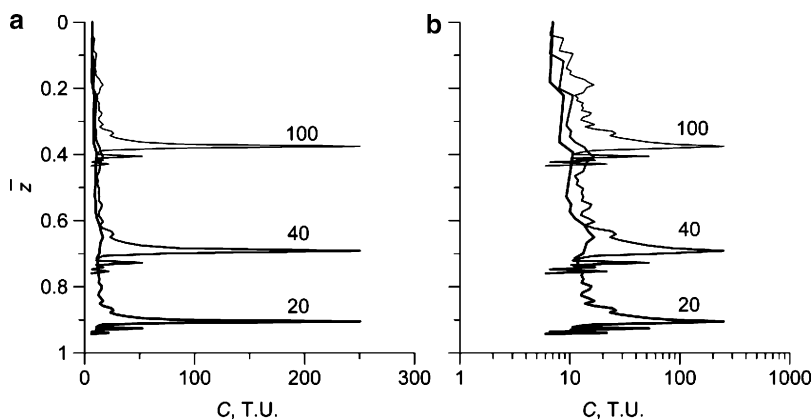


Fig. 4.3 Plots of function ${}^3\text{H}(z)$ at different values of τ_0 (year), constructed for 2010 for the input concentration signal in Fig. 3.9 (a and b are for linear and logarithmic scales on the abscissa, respectively)

to be very sensitive to the infiltration recharge rate. It can be easily seen that higher values of τ_0 ($\tau_0 \geq 100$ yr) cause the tritium wave to localize near groundwater table, while lower values of this parameter ($\tau_0 < 20$ yr) facilitate concentrating the major mass of tritium water near the aquifer bottom.

At the same time, this model yields relatively high peak values of tritium concentrations in groundwater (up to 300 T.U.), which are rarely recorded in nature, even when samples are taken in short intervals. To explain this contradiction, it is reasonable to consider models taking into account additional mechanisms of matter mixing due to dispersion.

4.3 Two-Layer Confined Aquifer

4.3.1 Model

Suppose that the transmissivities of the upper and lower layers (Fig. 4.4) are $T_1 = k_1 m_1$, $T_2 = k_2 m_2$ (where $T_1 + T_2 = T = \text{const}$), and their porosities are ϕ_1 и ϕ_2 ; the total flow discharge at the domain boundary (at $x = 0$) is $Q = Q_0$. The solution of the flow problem (under Dupuit–Forchheimer assumption) can be used to evaluate the components of specific discharge in each i th layer in j th zone:

$$\begin{aligned} q_{x_j}^{(i)} &= \frac{k_i}{T} (Q_0 + \varepsilon p), \\ q_{z_1}^{(1)} &= \varepsilon \left(1 - \frac{k_1}{T} z \right), \quad q_{z_1}^{(2)} = \varepsilon \left(1 - \frac{k_2(z - m_1) + k_1 m_1}{T} \right), \quad q_{z_2}^{(i)} = 0; \end{aligned} \quad (4.18)$$

here $p = x$ at $j = 1$ ($0 \leq x \leq a$) and $p = a$ at $j = 2$ ($a < x \leq L$).

The system of characteristic equations has the form:

$$\begin{aligned} \phi_i \frac{dx}{dt} &= q_{x_j}^{(i)}, \\ \phi_i \frac{dz}{dt} &= q_{z_j}^{(i)}. \end{aligned} \quad (4.19)$$

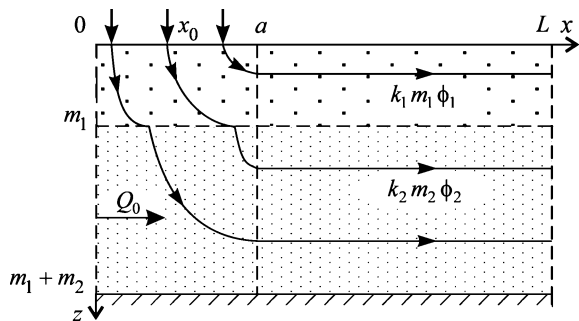


Fig. 4.4 Schematic cross-section of two-layer aquifer showing geometry of model domain, main parameters and flow-lines

Integrating these equations at $i = 1$, $j = 1$ over segments $[0, t]$, $[x_0, x]$ and $[0, z]$ yields the relationships

$$\begin{aligned}\bar{x} &= (\bar{x}_0 + \gamma) \exp\left(\frac{k_1 \varepsilon}{\phi_1 T} t\right) - \gamma, \\ \bar{z} &= \frac{T}{T_1} \left[1 - \exp\left(-\frac{k_1 \varepsilon}{\phi_1 T} t\right) \right],\end{aligned}\quad (4.20)$$

where $\bar{x} = x/a$, $\bar{z} = z/m_1$, $\gamma = Q_0/\varepsilon a$. Eliminating time from the expression, we obtain the equation of a flow line in the upper layer ($0 \leq \bar{z} \leq 1$):

$$\bar{z} = \frac{T}{T_1} \left(\frac{\bar{x} - \bar{x}_0}{\bar{x} + \gamma} \right). \quad (4.20a)$$

From here we can easily obtain the coordinates of characteristic points and the condition for the tagged particle to move from the first into the second layer:

$$\gamma \leq \frac{T_2}{T_1} (1 - \bar{x}_0) - \bar{x}_0, \quad (4.21)$$

or for the limiting (“neutral”, $\bar{x}_0 = 0$) flow line:

$$\gamma = Q_0/\varepsilon a \leq T_2/T_1.$$

The time for a tagged particle to reach the interface between the layers ($\bar{z} = 1$) is $t = \frac{\phi_1 T}{\varepsilon k_1} \ln\left(\frac{T}{T_1}\right)$. Considering the latter relationship, the solution of Eq. 4.19 becomes

$$\begin{aligned}\bar{x} &= (\bar{x}_0 + \gamma) \left(\frac{T}{T_2}\right)^{1 - k_2 \phi_1 / k_1 \phi_2} \exp\left(\frac{\varepsilon k_2}{\phi_2 T} t\right) - \gamma, \\ \bar{z} &= 1 + \bar{m}_2 \left[1 - \left(\frac{T}{T_2}\right)^{k_2 \phi_1 / k_1 \phi_2} \exp\left(-\frac{\varepsilon k_2}{\phi_2 T} t\right) \right],\end{aligned}\quad (4.22)$$

where $\bar{m}_2 = m_2/m_1$. From here we obtain the equation of the trajectory of particle motion in the lower layer ($1 \leq \bar{z} \leq 1 + \bar{m}_2$):

$$\bar{z} = 1 + \bar{m}_2 \left(1 - \frac{T}{T_2} \frac{\bar{x}_0 + \gamma}{\bar{x} + \gamma} \right). \quad (4.23)$$

The relationships (4.20a) and (4.23) were used to calculate the trajectories of particles along neutral flow lines originating from the point with coordinates (0, 0). As follows from Fig. 4.5, given the rate of infiltration and the values of a and Q , the character of subvertical motion of solute in the aquifer depends on the transmissivity

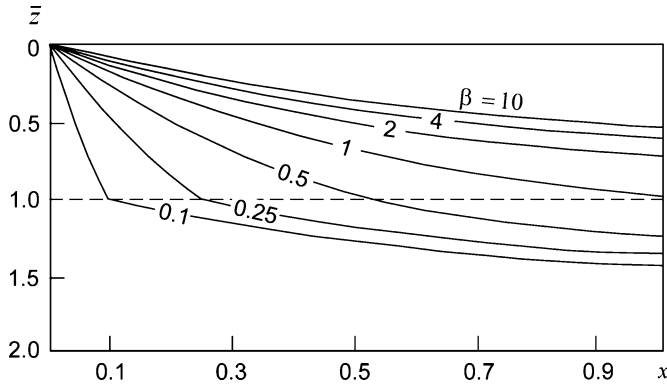


Fig. 4.5 Tagged-particle trajectories in a two-layer aquifer ($x_0 = 0$) at $\gamma = 1$, $m_1 = m_2$; figures at curves are the values of $\beta = T_1/T_2$

ratio of the upper to lower layer: the penetration depth decreases as the transmissivity of the upper layer increases relative to that of the lower layer. At the boundary of the infiltration domain (at $\bar{x} = 1$), waste penetration into the bed is estimated as

$$\begin{aligned} \bar{z}_a &= 1 + \bar{m}_2 \frac{1 - \beta\gamma}{1 + \gamma} \quad \text{at } \gamma < 1/\beta, \\ \bar{z}_a &= \frac{1 + \beta}{\beta(1 + \gamma)} \quad \text{at } \gamma > 1/\beta; \end{aligned} \quad (4.24)$$

here $\beta = T_1/T_2$, $\bar{m}_2 = m_2/m_1$.

The relationships given above allow one not only to outline the domain of groundwater pollution in the profile of the aquifer, but also to assess the tendencies in variations of decaying components. By using the time characteristics of solutions (4.20) and (4.22), by analogy with (4.13a), we obtain

$$C_1^i = \begin{cases} C_R \left(1 - \frac{T_1}{T} \bar{z} \right)^{\lambda \phi_1 T / k_1 \varepsilon} & \text{at } 0 \leq \bar{z} \leq 1 \quad (i = 1), \\ C_R \left[\left(\frac{T_2}{T} \right)^{k_2 \phi_1 / k_1 \phi_2} \left(1 - \frac{\bar{z} - 1}{\bar{m}_2} \right) \right]^{\lambda \phi_2 T / k_2 \varepsilon_R} & \text{at } 1 \leq \bar{z} \leq 1 + \bar{m}_2 \quad (i = 2). \end{cases} \quad (4.25)$$

Obviously, the solution (4.25) describes the concentration field behind the piston-like displacement front, whose position in any moment, t , for any trajectory (4.20a), (4.23) can be found from (4.20)–(4.22). Next, substituting the values $\bar{z} = \bar{z}_a(\bar{x}_0)$ into these relationships, we come to the concentration of components on the line $x = a$, bounding the solute source, $C_a^i = C_1^i|_{\bar{z}=\bar{z}_a}$. Now the solution for the second zone ($a < x \leq L$) becomes

$$C_2^i = C_a^i \exp \left[-\frac{\lambda(x-a) \phi_i T}{k_i(Q_0 + \varepsilon a)} \right]. \quad (4.26)$$

4.3.2 An Illustrative Example

The practical application of the theoretical concepts proposed here can be illustrated by the analysis of groundwater pollution by liquid phase of mining tailing pond in a mining area of the Kursk Magnetic Anomaly, Russian Federation. The two-layer section (Fig. 4.6a) is composed of water bearing chalk, underlain by sand rocks: the conditions on the boundaries of the flow domain and the relationships between parameters are given in the same figure. Note that the well defined block porosity of chalk rocks allowed us to assume that $\phi_1 = \phi_2$ for long (asymptotic) stages of transport. The steady-state concentration field (Fig. 4.6b) was calculated by the relationships (4.25) and (4.26) for nitrate ion ($\lambda = 5 \cdot 10^{-4} \text{ yr}^{-1}$).

It can be seen that appreciable denitrification of polluted water takes place even under the bed of the surface water body, where the vertical component of specific discharge contributes largely to the distribution of pollution. However, notwithstanding the considerable drop in concentration in sand layer near the inlet flow boundary, the pollution plume in sand is much better defined than in the chalk because of the higher sand permeability. Overall, the pattern of concentration isolines is complex and even somewhat paradoxical; it could have hardly been derived from simplified concepts, neglecting, in particular, the real character of specific discharge distribution in the heterogeneous aquifer. It is also clear that these results are of importance not only in forecasts, but also in the analysis (or planning) of hydrogeological monitoring data.

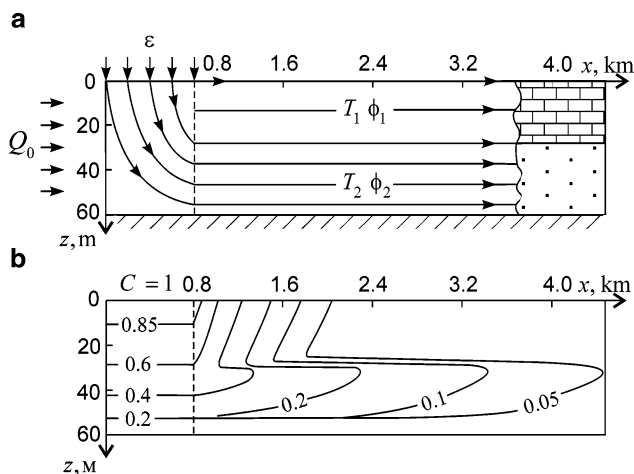


Fig. 4.6 On assessment of nitrate migration in the cross-section of two-layer water-bearing system (steady-state problem). **(a)** Schematic streamline structure and hydrogeological section with the input data: $\varepsilon = 0.011 \text{ m d}^{-1}$, $T_1 = 70 \text{ m}^2 \text{ d}^{-1}$, $T_2 = 350 \text{ m}^2 \text{ d}^{-1}$, $\phi_1 = 0.35$, $\phi_2 = 0.35$, $Q_0 = 2 \text{ m}^2 \text{ d}^{-1}$, $\lambda = 5 \cdot 10^{-4} \text{ d}^{-1}$; **(b)** contours of solute distribution (concentration isolines in relative units)

4.4 Multi-Layer (Stratified) Aquifer

The main difficulties in the theoretical analysis arise in studying groundwater flows and migration fluxes induced by area-distributed infiltration in thick (tens of meters) water-bearing strata with highly heterogeneous permeability. The variability of rock permeability in the vertical section determines the complex redistribution of regional groundwater flow between narrow local zones, which often weakly interact with one another. At the same time, the combination of stratified section, area-distributed infiltration recharge, and imperfect groundwater discharge contours causes strong differentiation of head in the vertical section (the head in the upper and lower flow zones in the section can differ by as much as many meters). Therefore, the migration analysis must be preceded by the hydrodynamic analysis of peculiar features of groundwater flow profile. The same order appears to be logical to use in presenting the material of this section.

4.4.1 Hydrodynamic Features of Flow

4.4.1.1 Flow in an Unconfined Semi-Infinite Aquifer

The specific discharge of an unconfined groundwater flow in horizontally stratified beds (Fig. 4.7) recharged by infiltration can be described by the equation

$$Q_x = Q_0 + \varepsilon x = -T_h \frac{dh}{dx}, \quad T_h = \int_0^h k(z) dz \quad (4.27)$$

(as before, the hydraulic gradient of flow is assumed to be independent of coordinate z —Dupuit–Forchheimer assumption); here h is groundwater flow depth, ε is specific infiltration rate, $k(z)$ is horizontal hydraulic conductivity in an elementary layer,

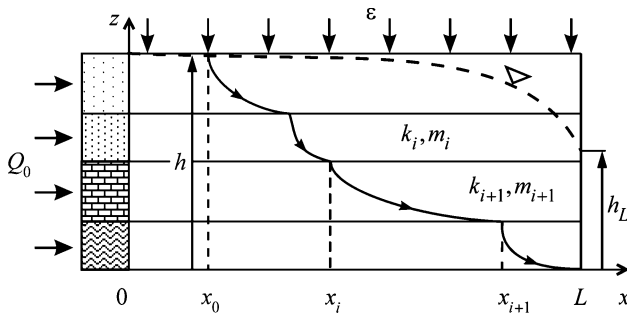


Fig. 4.7 Idealized cross-section for a layered aquifer showing a potential path for dissolved species migration

Q_0 is flow discharge at $x = 0$ (Fig. 4.7), such that when $Q_0 = 0$, $x = 0$ is a water divide line. The latter equality yields the expression for the horizontal Darcy velocity

$$q_x = -k(z) \frac{dh}{dx} = \varepsilon k(z) \frac{x + Q_0/\varepsilon}{T_h}. \quad (4.28)$$

Integrating the continuity equation for steady-state groundwater flow (4.2) with $q_z|_{z=0} = 0$ (note that the z -axis is directed vertically upward, Fig. 4.7) yields

$$q_z = - \int_0^z \frac{\partial q_x}{\partial x} dz = -\varepsilon \frac{T_h + \varepsilon(x + Q_0/\varepsilon)^2 k(h)/T_h}{T_h^2} \int_0^z k(z) dz. \quad (4.29)$$

The equality $dT_h/dh = k(h)$ was used in the derivation of the latter formula. With $k(z) = \text{const}$, $Q_0 = 0$ we arrive at the relationship (4.5b).

The formula (4.29) can be used to find the analytical expression describing vertical head distribution:

$$\Delta h_z = h - h_z = \varepsilon \left[\frac{T_h + \varepsilon(x + Q_0/\varepsilon)^2 k(h)/T_h}{T_h^2} \right] \int_z^h \left[\int_0^z k(\eta) d\eta \right] \frac{dz}{k(z)}. \quad (4.30)$$

Since $Q_x = -T_h \partial h / \partial x = -\partial G / \partial x$, the integral T_h and its derivative are related to *Girinski potential*, G (Girinski 1946a, b; Polubarinova-Kochina 1962; Bear 1972, p. 157; Shestakov 1995) by

$$T_h = \frac{dG}{dh}, \quad \frac{dT_h}{dh} = \frac{d^2 G}{dh^2}, \quad G = \int_0^h (h - z) k(z) dz. \quad (4.31)$$

This allows the solutions of unconfined flow problems in the potential function G for stratified beds to be used for evaluating flow process characteristics q_x , q_z , and Δh_z . For example, the boundary value problem is formulated as follows:

$$\frac{d^2 G}{dx^2} + \varepsilon = 0, \quad -\frac{dG}{dx} \Big|_{x=0} = Q_0, \quad G|_{x=L} = G_L; \quad (4.32)$$

and its solution is

$$G = G_L + \frac{\varepsilon}{2} (L^2 - x^2) + q_0(L - x). \quad (4.33)$$

Consider two typical situations corresponding to limiting structural models of stratified (flysch-like) formations (Fig. 4.8a, b).

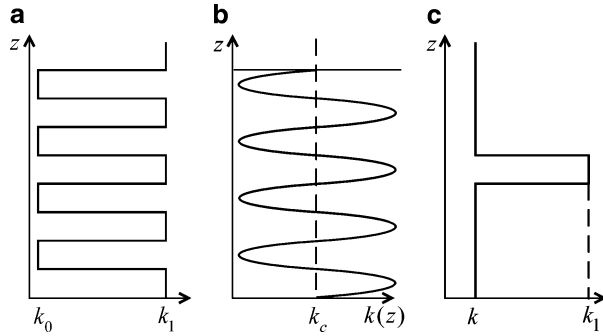


Fig. 4.8 Idealized permeability profiles: (a) a uniformly stratified bed, (b) a bed with sinusoidal variations in permeability over depth, (c) a bed including a high-permeability seam

In the case of uniformly stratified bed (Fig. 4.8a) with alternating high-permeability (k_1) and low-permeability (k_0) seams with the same thickness Δm ($\Delta m \ll m$, where m is the total thickness of the bed), $G \approx k_1 h^2 / 4$ and

$$y^2 = 1 + 2a(1 - \bar{x}^2) + 4b(1 - \bar{x}), \quad (4.34)$$

where $y = h/h_L$, $\bar{x} = x/L$, $a = \varepsilon L^2 / k_1 h_L^2$, $b = Q_0 L / k_1 h_L^2$. Further rearrangement of (4.30) yields

$$\Delta \bar{y}_z = \frac{\Delta h_z}{h} = \frac{\varepsilon}{4k_0} \left[1 + \frac{2a(1 + b/a)^2}{y^2} \right] (1 - \bar{z}^2), \quad \bar{z} = z/h. \quad (4.35)$$

As can be seen, considerable (a few meters to tens of meters, the total thickness of the groundwater flow being about 100 m) variations in $h(z)$ should be expected to occur in the section of layers with the hydraulic conductivity k_0 of the order of absolute values of infiltration recharge ε .

Now consider the stratified section (Fig. 4.8b) with harmonic variations of hydraulic conductivity over depth

$$k = k(z) = k_c \left(1 + W_m \sin \frac{2\pi z}{l_m} \right). \quad (4.36)$$

In this case we have

$$G = \frac{k_c h^2}{2} + \frac{k_c W_m l_m}{2\pi} h \left(1 - \frac{l_m}{2\pi h} \sin \frac{2\pi h}{l_m} \right), \quad (4.37)$$

where k_c is the mean hydraulic conductivity, l_m is the characteristic vertical scale, W_m is a parameter, characterizing the variation amplitude of bed permeability. When $y > y_L > 10$ ($y = 2\pi h / l_m$, $y_L = 2\pi h_L / l_m$), as is typical of the formulated problem (in the presence in the section of at least several zones associated with the rhythm

of rock permeability variations), the solution (4.34) is valid at $a = \bar{\varepsilon}L^2/2h_L^2$, $b = Q_0L/2k_ch_L^2$. Next, approximating the integral in (4.30) by the analytical formula

$$\int_z^h \left(\int_0^z k(\eta) d\eta \right) \frac{dz}{k(z)} = \left(\frac{l_m}{2\pi} \right)^2 \int_{\bar{z}}^y \frac{\bar{z} + W_m(1 - \cos \bar{z})}{1 + W_m \sin \bar{z}} d\bar{z} \\ \approx \left(\frac{l_m}{2\pi} \right)^2 \frac{y^2 - \bar{z}^2}{2.66\sqrt{1 - W_m}}, \quad \bar{z} = \frac{2\pi z}{l_m},$$

after some simple rearrangement, we obtain the solution of the problem ($Q_0 = 0$):

$$\Delta \bar{y}_z = \frac{y - y_z}{y} = \bar{\varepsilon} \frac{p^2 + g(1 + W_m \sin y)}{2.66p^3 \sqrt{1 - W_m}} (1 - (z')^2), \quad \bar{\varepsilon} = \frac{\varepsilon}{k_c}, \quad (4.38)$$

$$p = 1 + W_m(1 - \cos y)/y, \quad g = \frac{\bar{x}^2}{(1 - \bar{x}^2) + 1/a}, \quad z' = \frac{\bar{z}}{y} \equiv \frac{z}{h}, \quad \bar{x} = \frac{x}{L}.$$

At large y (areas near water divide):

$$\Delta \bar{y}_z = \frac{1 - (z')^2}{2.66\sqrt{1 - W_m}} \bar{\varepsilon}. \quad (4.38a)$$

Figure 4.9, illustrating variations in the relative head near bed bottom ($\Delta \bar{y}_0 = (y - y_0)/y \equiv \Delta \bar{y}_{z \max}$, $y_0 = y|_{z=0}$) in the direction of flow x , gives an estimate of the possible range of variations of head at different values of parameter W_m and dimensionless group a . The amplitude of these variations can be seen to increase with observational point approaching the groundwater flow discharge area ($x = L$). The oscillation frequency depends on parameter a , characterizing the extent to which the flow is unconfined. The mean vertical drop in head is governed by parameter W_m .

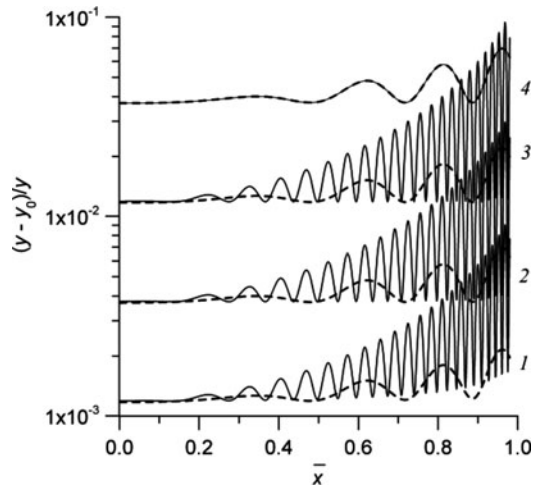


Fig. 4.9 Variations in the relative vertical head differentials in an unconfined bed with sinusoidal variations in permeability over depth: $y_L = 100$, $\varepsilon/k_c = 0.001$, $a = 5$ (full curves) and $a = 0.5$ (dashed curves); 1–4: $(1 - W_m) = 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}$

Thus, theoretical analysis suggests that harmonic head oscillations (measured at about the same absolute elevations) can take place in the vicinity of near-surface groundwater discharge zones in unconfined infiltration-type groundwater flows in thick strata of flishoid type. This is due to the depression surface successively crossing rock beds with radically different hydraulic conductivity values.

4.4.1.2 Flow in a Confined Semi-Infinite Aquifer

With $dT_h/dh \rightarrow 0$ (see Eqs. 4.28–4.30), we obtain formulas for a confined flow:

$$q_x = \varepsilon \frac{k(z)}{T} (Q_0/\varepsilon + x), q_z = -\varepsilon \frac{T_z}{T}, \quad (4.39)$$

$$H_z = H_0 - \frac{\varepsilon}{T} \int_z^m \frac{T_z}{k(z)} dz, T_z = \int_0^z k(\xi) d\xi, \quad (4.40)$$

where T is the total transmissivity of the bed, H_0 is the head at the bed top (at $z = m$). In the second formula (4.39), Darcy velocity q_z corresponds to the recharge reaching an elementary layer with vertical coordinate z . Clearly, such passage to the limit is exact enough for water-divide areas, where the slope of phreatic flow table is relatively small.

4.4.1.3 An Example of Field Data Analysis

The hydrodynamic properties of stratified near-surface aquifers considered above can be illustrated based on data of field studies carried out in the southeaster Tatarstan, Russian Federation. A typical hydrogeological section is given in Fig. 4.10, presenting a head distribution in a stratum of deposits of Kazan stage of Upper Permian, which is typical of basins with infiltration groundwater recharge. This stratum (its thickness can be as large as 200 m near water divide) is represented by terrigenous-carbonate deposits (frequent, irregular intercalation of sandstones, limestones, and argillites with the thickness of each layer commonly not exceeding a few meters).

Plots in Fig. 4.11 are some generalization of groundwater head distribution, illustrating groundwater head drop from top to bottom in the section of Kazan deposit strata; they are constructed based on materials of hydrogeological drilling near Aleksandrovskii Settlement and in Al'met'evskii district.

Such distribution of heads ensures the penetration of pollution from the surface to large depth in the presence of clay beds (relatively impervious), which are sufficiently numerous and continuous in the section. This can be seen from data of interval hydrochemical and soil sampling. Overall, the analysis shows that, in a multilayer stratum with rhythmical alternation of layers with high (k) and low (k_0) permeability (with $k_0/k \ll 1$), significant (several meters to a few tens of meters) vertical head differentials appear at $\varepsilon/k_0 > 1.5 - 2$.

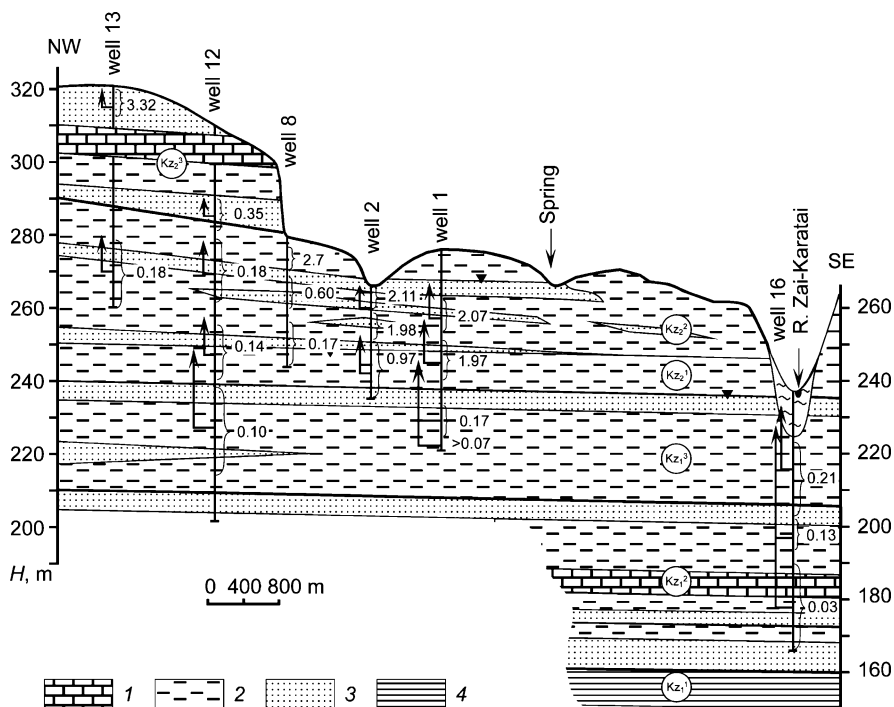


Fig. 4.10 Typical hydrogeological section of the aquifer system of Kazan deposits. *Arrows* show the standing groundwater level; figures *right* of the denoted intervals are chloride content of water, g/L. (1) Carbonate rocks, (2) aleurolites, (3) sandstones, (4) lingule clays (regional aquiclude)

4.4.2 Characteristic-Based Relations

4.4.2.1 Basic Equations

The trajectories of solute particle motion in a stratified bed (see Fig. 4.7), as well as the time (kinematic) characteristics of the process are determined by the solution of system (4.3). Thus, dividing the right and left parts of equations of the system (4.3), respectively, we obtain the equation

$$q_z/q_x = dz/dx. \quad (4.41)$$

Its integration for the case of an *unconfined* flow conditions (with the Darcy velocity components q_x and q_z determined from Eqs. 4.28 and 4.29) yields the relationship for determining the characteristic $x(z)$, i.e., the coordinate of the flow line originating from the point $x_0(h)$ on the flow surface:

$$\int_h^z \frac{k(z)}{T_z} dz = -\ln \frac{x + Q_0/\varepsilon}{x_0(h) + Q_0/\varepsilon} - \varepsilon \int_{x_0(h)}^x \frac{(x + Q_0/\varepsilon)k(h)}{T_h^2} dx; \quad (4.42)$$

solutions (4.44) and (4.45) can be rewritten in the finite-differential form (the layers are numbered from top to bottom):

$$\frac{x_i + Q_0/\varepsilon}{x_0 + Q_0/\varepsilon} = \frac{T}{T - T_{m-z}}, \quad (4.46)$$

$$t_i = \frac{1}{\varepsilon} \sum_{i=1}^i \frac{m_i \phi_i T}{T_i} \ln \left(1 + \frac{T_i}{T - T_{m-z}} \right), \quad (4.47)$$

where $T_{m-z} = \sum_{j=1}^i T_j$, $T_j = k_j m_j$; the upper limit of summing in (4.47) corresponds to the number of the model layer; the inner index (i) is current layer's number.

4.4.2.2 Synthesized Examples

Consider the migration process taking place in different types of hydrogeological sections and groundwater flow regimes. The first type of section is represented by a stratum with sinusoidal variations of permeability over depth (the flow is unconfined); the second type is represented by a medium-permeability (k) stratum including a high-permeability layer k_1 (confined flow); and the third type is a fractured rock stratum with permeability decreasing with depth.

The first example. Numerical methods are used to calculate the integral functions in (4.42) and (4.43), where the unconfined character of groundwater flow is taken into account explicitly for a medium with wide sinusoidal oscillation of hydraulic conductivity (Eq. 4.36, Fig. 4.8b). The graphical representation of the solution for particular values of parameter $a = \varepsilon L^2 / k_c h_L^2$ at $W_m = 0.999$ is given in Fig. 4.12. This plot can be characterized by the dimensionless time required for the tagged particle that entered the bed in the point $\bar{x}_0 = x_0/L$ to reach the outlet flow section

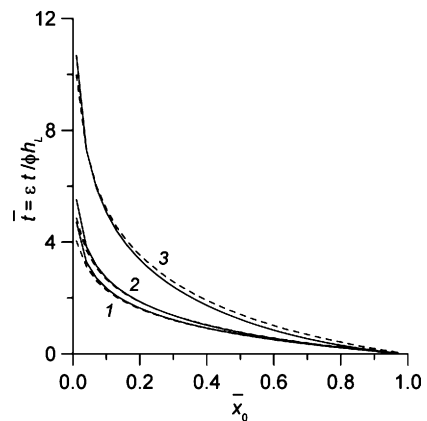


Fig. 4.12 Variations in the characteristics of an unconfined flow in a water-bearing stratum with sinusoidal variations in hydraulic conductivity over depth. *Full* curves are for $(1-W_m) = 1.0$ (homogeneous bed), *dashed* curves are for $(1-W_m) = 0.0001$. $(l-3)-a = 0.05, 0.5$ and 5 , respectively

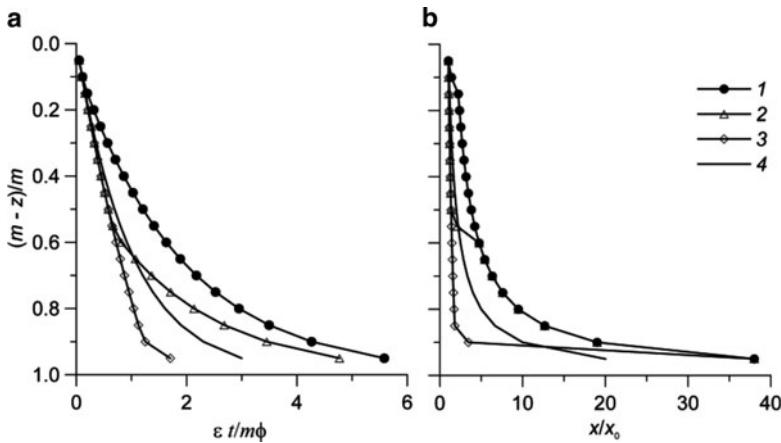


Fig. 4.13 Plots of characteristics (a) $i(\bar{z})$ and (b) $\bar{x}(\bar{z})$ for a water-bearing strata containing a high-permeability seam ($m = 50$ m, $m_1/m = 0.1$). (1, 2, 3) The top, bottom, and middle parts of the bed, respectively; (4) homogeneous bed

($\bar{x}_0 = 1$, $h = h_L$), located at a distance L from the water divide. The migration process is seen to be slightly sensible to variations in the hydraulic conductivity in the section.

The second example. This example reflects the comparison of calculations having been carried out for a homogeneous confined bed (with a total transmissivity of $T = 19 \text{ md}^{-1} \times 50 \text{ m} = 95 \text{ m}^2 \text{ d}^{-1}$) with calculations for a bed with equivalent transmissivity, containing a high-permeability zone (see Fig. 4.8c) $T_1 = k_1 m_1$ with a thickness of $m_1 = 0.1m = 0.1 \times 50 \text{ m} = 5 \text{ m}$. In this case it was assumed that $k_1/k = 10$ ((10 m/day)/(1 m/day)). The estimates were obtained for variants with the high-permeability layer lying near the bed roof, in its middle part, and near its bottom. Calculation results are also given as plots of characteristics (Fig. 4.13).

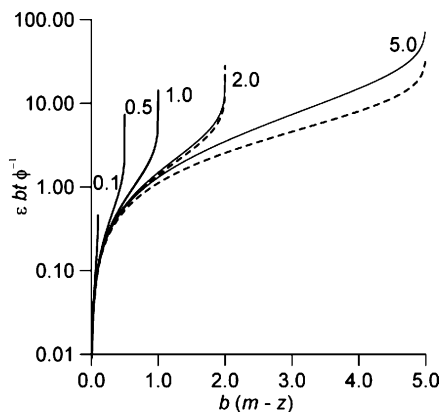
The averaging of the strata permeability over the section yields the model characteristics of the process, which appreciably differ from the “real” values, i.e., those obtained in the presence of a zone of focusing of the groundwater flow; the hypsometric position of this zone in the section also has its effect.

The third example. In fissured rocks, the general trend toward a decrease in permeability and the density of fissures in the rock should be taken into account. To assess the role of these factors, we use formula (4.45), assuming the hydraulic conductivity to exponentially decline with depth and to be a power function of fracture density:

$$\frac{k}{\bar{k}} = \exp[-b(m-z)], \quad \frac{\phi}{\bar{\phi}} = \left(\frac{k}{\bar{k}}\right)^a, \quad (4.48)$$

where $\bar{k}$ and $\bar{\phi}$ are the mean values of parameters near bed roof, b and a are empirical coefficients (commonly, $1/3 < a < 1$). The results of numerical integration of formula (4.45) with $a = 1/2$ are plotted in Fig. 4.14.

Fig. 4.14 Flow characteristics in a fissured stratum with rock permeability and fissure density declining with depth; $y_0 = bm$, $a = 1/2$; dashed lines are for calculations with averaged parameters



The plots show that the deviation of curves calculated in the model with varying parameters (4.48) from curves obtained with $k = \bar{k}$, $\phi = \bar{\phi}$ is significant when $y_0 > y > 3 - 5$ ($y_0 = bm$, $y = b(m - z)$). This corresponds to the case when pollutant migration is predicted in rocks with fissure density attenuation with depth characterized by large constants b .

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Chapter 5

Models for Assessment of Transverse Diffusive and Advective Transfer in Regional Two-Layer Systems

In many groundwater systems, the porous media have near-horizontal layered structures that have been formed by natural sedimentology processes. Diffusive transfer of solute mass between layers differing in hydraulic conductivity is a key smoothing mechanism of concentration profiles in such stratified groundwater systems. A result of this process is the higher rate of mass transfer in layers with lower permeability and its lower rate in layers with higher permeability.

Solute transport models for idealistic stratified multi-layer systems, originally developed in the 1970s–1980s, served as a starting point in the analysis of the scale-dependent dispersive phenomenon in real aquifer systems (Gelhar et al. 1979; Matheron and de Marsily 1980; Dagan 1982; Molz et al. 1983; Güven et al. 1984). It was shown that macrodispersivity, a macroscopic analogue to microdispersivity in the Fickian transport equation, has an advective component, which is caused by the velocity variations, $u(z)$, combined with vertical mixing determined by molecular diffusion and local transverse hydrodynamic dispersion. However, the real, asymptotic, Fickian conditions are rarely reached. Expressions obtained for macrodispersivity illustrate the scale-dependent (time-dependent) behavior of this parameter.

In this chapter, we review some important features of the transport process in two-layer systems, which are of special interest for *regional-scale assessments*, and present an illustrative example from real hydrogeological practice to demonstrate the application of the modeling concept.

There exist a large number of models describing the capacitance effect of low-permeability layers owing to their ability to store and release solute due to interlayer diffusive transfer and exchange. Among the best known and developed are two-dimensional diffusive (Skopp and Warrick 1974; Barker 1982; Leij and Van Genuchten 1995; Ling et al. 2002), quasi-one-dimensional first-order-rate (Hantush and Mariño 1998) and utmost asymptotic (Marle et al. 1967; Marinosehi et al. 1998) models which can be applied to analyzing different stages of solute transport in multi-layer systems.

Less developed are models for multi-layer leaky aquifer systems where the role of transverse advective-diffusive transfer of solutes is to be identified for groundwater quality trend assessment and prediction at the regional scale. Therefore, in this chapter, we will specially focus on mathematical formulation and solution of a

solute transport problem related to a two-layer aquifer system, represented by the aquifer and adjoining leaky stratum which should be identified as leaky aquiclude.

5.1 Diffusion-Dispersion Interlayer Exchange

In the general case, models for describing solute migration in stratified groundwater systems without crossflow are based on the equation (Molz et al. 1983; Güven et al. 1984)

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x}(u_x C) - \frac{\partial}{\partial x} \left(D_x \frac{\partial C}{\partial x} \right) - \frac{\partial}{\partial z} \left(D_z \frac{\partial C}{\partial z} \right) = 0, \quad (5.1)$$

where all parameters are deterministic functions of the vertical coordinate, z .

The simplest example of a deterministic stratified system is a two-layer confined reservoir (Fig. 5.1). In a reasonably simplified mathematical model of such reservoir, the main migration mechanisms are (1) advective solute transport, whose intensity can be characterized by flow velocities in individual layers $u_{x1} = q_{x1}/\phi_1$ and $u_{x2} = q_{x2}/\phi_2$ (subscripts 1 and 2 refer to layers with higher and lower permeability, respectively), and (2) transverse dispersion (diffusion) in the less permeable layer, characterized by a constant coefficient D_{z2} . The vertical concentration gradient in the more permeable layer, the advective exchange between layers, and the longitudinal dispersion in both layers are neglected at this stage. The assumptions made here allow us to represent Eq. 5.1 with variable coefficients as the system of two interrelated equations with constant coefficients:

- solute mass balance equation in layer 1

$$\frac{\partial C_1}{\partial t} + u_{x1} \frac{\partial C_1}{\partial x} + \frac{W_s}{\phi_1} = 0; \quad (5.2)$$

- equation of advective transport with transverse dispersion in layer 2

$$\frac{\partial C_2}{\partial t} + u_{x2} \frac{\partial C_2}{\partial x} - D_{z2} \frac{\partial^2 C_2}{\partial z^2} = 0, \quad (5.3)$$

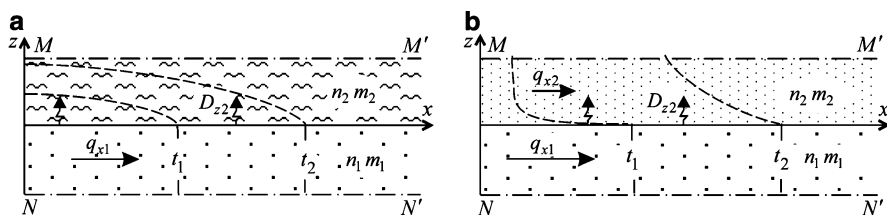


Fig. 5.1 Schematic diagrams of two-layer flow systems. (a) Two-layer bed with radically different permeabilities of individual layers; (b) the same with comparable permeability values. The horizontal and vertical arrows show the directions of advective and diffusion–dispersion fluxes; $M-M'$ and $N-N'$ are the boundaries of the model element

where W_s is the specific (per unit thickness) mass exchange rate:

$$W_s = -\frac{\phi_2 D_{z2}}{m_1} \frac{\partial C_2}{\partial z} \Big|_{z=0}. \quad (5.4)$$

Equations 5.2–5.3 are supplemented by the following initial and boundary conditions:

$$\begin{aligned} C_1|_{t=0} = C_2|_{t=0} = 0, \quad C_1|_{x=0} = C_2|_{x=0} = C_0, \\ C_1|_{z=0} = C_2|_{z=0}, \quad \frac{\partial C_1}{\partial z} \Big|_{z=-m_1-0} = \frac{\partial C_2}{\partial z} \Big|_{z=m_2} = 0. \end{aligned} \quad (5.5)$$

5.1.1 Balance Estimation for Layer-by-Layer Mass Transport Scheme

Clearly, the first stages of migration in a two-layer reservoir involve independent (layer-by-layer) transport, when the interaction of layers has practically no effect on the propagation velocity of the contacting solutions in each layer. Therefore, the coordinates of fronts can be calculated by using a piston-like displacement scheme, and the size, Δx^* , of the zone between the fronts grows in proportion to the current time of the process and the difference between flow velocities in the two layers:

$$\Delta x^* = (u_{x1} - u_{x2}) t. \quad (5.6)$$

The most illustrative estimates for validating the calculation scheme of layer-by-layer transport can be derived from balance considerations, stemming from the solution of the boundary problem (5.2)–(5.5) for zero spatial moment of the concentration distribution (Mironenko and Rumynin 1986):

$$\phi_1 \int_0^\infty C_1 dx = M_0(t) - M_d(t), \quad (5.7)$$

$$M_0(t) = \phi_1 C_0 u_{x1} t, \quad M_d(t) = \phi_1 C_0 (u_{x1} - u_{x2}) \left(1 - \frac{W}{Bt}\right) t, \quad (5.7a)$$

$$W = 2\sqrt{\frac{Bt}{\pi}} + e^{Bt} \operatorname{erfc}\sqrt{Bt} - 1, \quad B = \frac{D_{z2}\phi_2^2}{m_1^2\phi_1^2}. \quad (5.7b)$$

The solution (5.7) was sought for under the assumption that the limited thickness of the less permeable layer has no effect on the rate of transverse displacement within the zone between fronts; considering the initial stage of the process, we can assume that this limitation is not crucial.

The left part of formula (5.7) gives the total amount of solute in the more permeable layer (converted to unit flow thickness). The right part of Eq. 5.7 contains two mass balance components: M_0 is the total amount of solute that entered through the inlet boundary of the more permeable layer during time t , and M_d is the amount of solute that diffused from this layer into the less permeable layer during the same time. It is reasonable to assume that the regime of layer-by-layer transfer exists while the ratio M_d/M_0 is small:

$$\frac{M_d}{M_0} = \frac{u_{x1} - u_{x2}}{u_{x1}} \left(1 - \frac{W}{Bt} \right) < \varepsilon. \quad (5.8)$$

For the least favorable case where $u_{x1} \gg u_{x2}$, we find that the applicability condition for the layer-by-layer transport scheme at $\varepsilon = 0.1$ will be true when $Bt < 0.5$ or

$$t < t_d \approx 0.05 \frac{m_1^2 \phi_1^2}{D_{z2} \phi_2^2}. \quad (5.8a)$$

From here we obtain, in particular, that for a section represented by alternation of beds of sand–clay rocks with a thickness of the order of 1 m, the time t_d is commonly several hundreds of days; for a thin-layer structure, where the thickness of individual layers does not exceed a few tens of centimeters, the time t_d varies from a few days to several tens of days.

Below, when considering migration in a two-layer reservoir not within the time frame (5.8) or (5.8a), we will restrict our consideration to the cases allowing limiting (asymptotic) solution.

5.1.2 A Case of Two-Layer Stratum with Sharp Permeability Contrast Between Layers

This case can be described by the system of Eqs. 5.2–5.5 with $u_{x2} = 0$, so that the transverse mass exchange is controlled by the pore diffusion coefficient ($D_{z2} = D_m$).

5.1.2.1 Complete Solution of the Problem

Converted into Laplace images with zero initial conditions, the system of Eqs. 5.2–5.3 becomes

$$p\tilde{C}_1 + u_{x1} \frac{d\tilde{C}_1}{dx} - \frac{D_m \phi_2}{m_1 \phi_1} \frac{d\tilde{C}_2}{dz} \Big|_{z=0} = 0, \quad (5.9)$$

$$p\tilde{C}_2 - D_m \frac{d^2 \tilde{C}_2}{dz^2} = 0. \quad (5.9a)$$

The boundary conditions (5.5) are transformed accordingly.

The general solution of the diffusion Eq. 5.9a has the form (Kamke 1977; Polyenin and Zaitsev 2003):

$$\tilde{C}_2 = A \operatorname{ch}[\sqrt{\bar{p}}(1 - z/m_2)] + B \operatorname{sh}[\sqrt{\bar{p}}(1 - z/m_2)], \quad (5.9b)$$

where $\bar{p} = m_2^2 p / D_m$, A and B are integration constants. The last boundary condition in (5.5) is satisfied only when $B = 0$. The integration constant A is determined from the condition (5.5) of concentration continuity on the boundary between layers. The solution of Eq. 5.9a is

$$\tilde{C}_2 = \frac{\operatorname{ch}[\sqrt{\bar{p}}(1 - z/m_2)]}{\operatorname{ch}\sqrt{\bar{p}}} \tilde{C}_1. \quad (5.9c)$$

The concentration gradient on the boundary between layers

$$\left. \frac{d\tilde{C}_2}{dz} \right|_{z=0} = -\tilde{C}_1 \sqrt{\frac{p}{D_m}} \operatorname{th}(\sqrt{\bar{p}}). \quad (5.9d)$$

In this case the advection Eq. 5.9 in the high-permeability layer becomes

$$\left[p + \frac{\phi_2}{m_1 \phi_1} \sqrt{D_m p} \operatorname{th}(\sqrt{\bar{p}}) \right] \tilde{C}_1 + u_{x1} \frac{d\tilde{C}_1}{dx} = 0. \quad (5.9e)$$

Its solution under the condition of constant concentration $\tilde{C}_1 = C_0/p$ on the boundary $x = 0$ (5.5) can be obtained by separation of variables

$$\tilde{C}_1 = \frac{C_0}{p} \exp \left[-\frac{x}{u_{x1}} \left(p + \frac{G_p}{\phi_1} \right) \right], \quad (5.10)$$

or in a more general form

$$\tilde{C} = \frac{C_0 \operatorname{ch}[\sqrt{\bar{p}}(1 - z/m_2)]}{p \operatorname{ch}\sqrt{\bar{p}}} \exp \left[-\frac{x}{u_{x1}} \left(p + \frac{G_p}{\phi_1} \right) \right], \quad (5.10a)$$

where $\tilde{C}|_{z=0} \equiv \tilde{C}_1$; $\tilde{C}|_{z>0} \equiv \tilde{C}_2$;

$$G_p = \frac{\phi_2 D_m \sqrt{\bar{p}}}{m_1 m_2} \operatorname{th}\sqrt{\bar{p}}, \quad \bar{p} = \frac{m_2^2 p}{D_m}. \quad (5.10b)$$

The solution of such problems in Laplace transforms can easily take into account the longitudinal hydrodynamic dispersion (Maloszewski and Zuber 1983)

$$\tilde{C}_1 = \frac{C_0}{p} \exp \left\{ \frac{\operatorname{Pe}}{2} \left[1 - \sqrt{1 + \frac{4t_0}{\operatorname{Pe}} \left(p + \frac{G_p}{\phi_1} \right)} \right] \right\}, \quad (5.10c)$$

and the decay (destruction) of the component (Ling et al. 2002)

$$\tilde{C}_1 = \frac{C_0}{p} \exp \left\{ \frac{\text{Pe}}{2} \left[1 - \sqrt{1 + \frac{4t_0}{\text{Pe}} \left((p + \lambda) + \frac{G_{(p+\lambda)}}{\phi_1} \right)} \right] \right\}; \quad (5.10d)$$

here $t_0 = x/u_{x1}$, $\text{Pe} = u_{x1}x/D_L$, D_L is the coefficient of longitudinal hydrodynamic dispersion in the high-permeability layer, λ is decay constant; function $G_{(p+\lambda)}$ is determined by (5.10b), where parameter p is replaced by $p + \lambda$. With $D_L \rightarrow 0$ and $\lambda \rightarrow 0$, the solutions (5.10c) and (5.10d) turn into formula (5.10). In the original formulation of the problem (Maloszewski and Zuber 1983; Ling et al. 2002), the process of solute transport in a single fissure (in contact with a porous rock matrix) was considered, in which, unlike a porous stratified system, the dispersion component can play a significant role in small-scale tracer experiments.

The inversion of the formula (5.10) for concentration in the high-permeability layer yields the following solution (Roshal 1969; Skopp and Warrick 1974; Barker 1982; Ling et al. 2002):

$$\begin{aligned} \bar{C}(\eta, \tau) = & \frac{1}{2} + \frac{2}{\pi} \int_0^\infty \exp \left[-\frac{1}{2} \eta y \frac{\text{sh}(y) - \sin(y)}{\text{ch}(y) + \cos(y)} \right] \\ & \times \sin \left[\frac{1}{2} \tau y^2 - \frac{1}{2} \eta y \frac{\text{sh}(y) + \sin(y)}{\text{ch}(y) + \cos(y)} \right] \frac{dy}{y}, \end{aligned} \quad (5.11)$$

written in the dimensionless form; here

$$\eta = \frac{x D_m \phi_2}{u_{x1} m_1 m_2 \phi_1}; \quad \tau = \frac{D_m}{m_2^2} \left(t - \frac{x}{u_{x1}} \right), \quad (5.11a)$$

$\bar{C}(\eta, \tau) \equiv \tilde{C}_1(\eta, \tau) = C_1(\eta, \tau)/C_0$, y is dimensionless integration variable. The solution (5.11) is plotted in Fig. 5.2. Numerical methods should be used to invert formula (5.10c) (Reimus et al. 2003).

5.1.2.2 Asymptotic Solutions

Analysis of solutions in images (5.10)–(5.10a) allows us to obtain solutions more convenient for practical use. Thus, parameter G_p at large values of dimensionless group $\bar{p}$, which correspond to initial time moments, tends to the limit $G_p \approx (p D_m)^{1/2} \phi_2 / m_1$, at which the image function (5.10a) has the tabulated original (Bateman and Erdelyi 1954):

$$\bar{C} = \text{erfc} \left\{ \frac{z + D_m \phi_2 x / m_1 \phi_1 u_{x1}}{2 [D_m (t - x/u_{x1})]^{1/2}} \right\}. \quad (5.12)$$

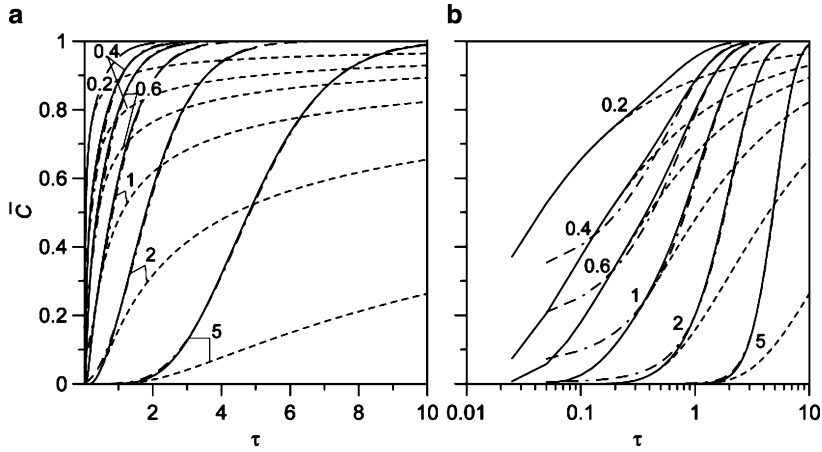


Fig. 5.2 Exact and approximate solutions of migration problem in a two-layer system. Eq. 5.11 (exact solution) – full lines; Eq. 5.13 – dashed lines; Eq. 5.16 with η , τ and α_s , determined according to (5.18) and (5.18a), – dash-and-dot lines. Figures at the curves are the values of η . (a) and (b) are the linear and logarithmic scales on the abscissa

This solution, written in solute concentration in the high-permeability layer ($\bar{C} \equiv \bar{C}_1$ at $z = 0$), is known as *Lauverier formula (solution)* (Lauverier 1955). In dimensionless form, the Lauverier solution becomes

$$\bar{C} = \operatorname{erfc} \left(\frac{\eta}{2\sqrt{\tau}} \right), \quad (5.13)$$

where η and τ are determined by (5.11a). The solution (5.13) is plotted in Fig. 5.2.

The assumption that the process is of short duration meets the physical assumption of *unlimited low-permeability layer space for diffusion* (or *unlimited diffusion capacity*), suggesting that the diffusing components will not reach its outer boundary within the period under consideration. This assumption can be considered certainly valid when

$$\tau = D_m t_c / m_2^2 < 0.3 \div 0.5, \quad (5.14)$$

where time t_c is measured from the moment t_0 when the front of piston-like displacement will arrive at the point in question ($t_c = t - t_0$). The criterion (5.14) is confirmed by the correlation of the exact (5.11) and approximate (5.12) solution of the migration problem (Fig. 5.2).

Another limiting value G_p can be obtained with relatively small values of $\bar{p}$ group, i.e., for large time moments: $G_p \approx (2\phi_2 D_m / m_1 m_2) p / (p + 2D_m / m_2^2)$. In this case, the solution in Laplace transforms can be written in the dimensionless form

$$\tilde{C}(\eta, \bar{p}) = \left[\frac{1}{\bar{p}} \exp \left(-\eta \frac{\bar{p}}{1 + \bar{p}} \right) \right] \exp(-\tau_0 \bar{p}), \quad (5.15)$$

where $\bar{p} = pm_2^2/2D_m$, $\eta = 2\phi_2 D_m t_0 / m_1 m_2 \phi_1$, $\tau_0 = 2D_m t_0 / m_2^2$. Finally we take the inverse Laplace transform of the expression in square brackets (Sect. 6.1.3.3) to obtain the solution in which the exponent $\exp(-\tau_0 \bar{p}) = \exp(-pt_0)$ introduces a time lag

$$\bar{C} = J(\eta, \tau) = 1 - e^{-\tau} \int_0^\eta e^{-\lambda} I_0 \left(2\sqrt{\tau\lambda} \right) d\lambda, \quad (5.16)$$

where

$$\bar{C} \equiv \bar{C}, \quad \eta = \frac{\phi_2 D_m t_0}{m_1 \phi_1 (m_2/2)}, \quad \tau = \frac{D_m}{m_2 (m_2/2)} (t - t_0), \quad (5.16a)$$

here $I_0(z)$ is modified zero-order Bessel function of the first kind. The properties of function $J(\eta, \tau)$ are discussed in Sect. 6.1.3.3. It is also plotted there. The ratio $m_e = m_2/2$ can be taken as the characteristic (effective) transport length in the low-permeability layer.

The obtained result is also of interest because a similar solution has been derived from a physical assumption of a spatially uniform concentration distribution in the low-permeability layer through the transient process, $C_2(z, t) \approx C_2(t)$, corresponding to the *lumped capacitance model*. This model suggests that the entire capacitance of the low-permeability layer is concentrated in its middle plane (here the concentration corresponds to the mean value $C_2 = C_2(t)$), and the rate of interlayer exchange W_s is determined by a quasi-steady regime

$$\frac{W_s}{\phi_1} = \sigma \alpha_s (C_1 - C_2); \quad \frac{\partial C_2}{\partial t} = \alpha_s (C_1 - C_2), \quad (5.17)$$

where α_s is interlayer exchange coefficient; $\sigma = m_2 \phi_2 / m_1 \phi_1$; the second Eq. 5.17 corresponds to the solute balance condition in the low-permeability layer. The general solution of the problem (5.2), (5.17) for solute concentration in the high-permeability layer C_1 is described by (5.16) with arguments

$$\eta = \sigma \alpha_s t_0, \quad \tau = \alpha_s (t - t_0). \quad (5.18)$$

The formal comparison of those variables with (5.16a) readily yields the expression for interlayer exchange coefficient $\alpha_s \approx 2D_m/m_2^2$. The comparison with the exact solution of the transport problem in a two-layer bed (Fig. 5.2) shows that somewhat better result can be obtained with

$$\alpha_s \approx 3D_m/m_2^2, \quad (5.18a)$$

i.e., the effective length m_e amounts to about one-third of the thickness of the low-permeability layer.

Further analysis shows that, as applied to the fundamental problem, the lumped capacitance model yields relatively reliable results under the conditions

$$\alpha_s t_c > 0.5 - 1.0, \quad x < x_{01}/(1 + \sigma), \quad (5.19)$$

where x_{01} is the coordinate of piston-like displacement front in the high-permeability layer ($x_{01} = u_{x1}t$). The second condition in (5.19) is satisfied by the concentration points characterizing the rear half of the indicator wave ($\bar{C} \geq 0.5$).

During the very long migration stages, when

$$\alpha_s t_c \gtrsim 10, \quad (5.20)$$

which corresponds to the *limiting – asymptotic* transport regime, the solutions for macroscopic advection–dispersion equation,

$$\frac{\partial C}{\partial t} + u^* \frac{\partial C}{\partial x} - D_L^* \frac{\partial^2 C}{\partial x^2} = 0, \quad (5.21)$$

are valid with apparent or asymptotic coefficients

$$u^* = \frac{u_{x1}}{(1 + \sigma)}, \quad D_L^* = \frac{\sigma}{\alpha_s(1 + \sigma)} (u^*)^2; \quad (5.21a)$$

here D_L^* is the coefficient of asymptotic macrodispersion, derived under the condition $D_{z1} \gg D_{z2}$. Note the quadratic dependence of the macrodispersion coefficient on flow velocity, $D_L^* \sim u_{x1}^2$ (unlike the microdispersion coefficient D_L).

Numerical estimates show that for $\bar{C} > 0.5$, the asymptotic diffusion model also yields quite acceptable results under less rigid time criterion $\alpha_s t_c > 3 - 5$, which does not radically differ from the applicability condition (see the first criterion in (5.19)) for the lumped capacitance model. Thus, the latter model is a transient modeling approximation between two extreme asymptotic regions, satisfying covering a much wider range of practical problems.

5.1.3 The Case of a Reservoir Consisting of Two Permeable Layers

In this case (see Fig. 5.1b) we restrict ourselves to the analysis of an approximate solution (Mironenko and Rumynin 1986) for long enough migration stages with quasi-steady mass-exchange regime. In accordance with this, we come to an approximate relationship for the relative displacement of fronts (i.e., the boundaries of zones of complete saturation by the solute) in the interacting layers

$$\Delta x^* \approx (u_{x1} - u_{x2})(1 - e^{-t/\tau_s})\tau_s, \quad (5.22)$$

$$\tau_s = \frac{1}{\alpha_s(1 + \sigma)}, \quad (5.22a)$$

where τ_s is the characteristic relaxation time of the two-layer system (it corresponds to the period of complete involvement of the bed in the processes of transverse dispersion mixing). Analysis of (5.22) shows that the relative displacement of fronts is

proportional to the difference between the flow velocities in the layers and increases over time, however, approaching at $t > (2 - 3)\tau_s$ its limiting value

$$\Delta x^* \approx (u_{x1} - u_{x2})\tau_s; \quad (5.23)$$

in this case, the further increase in the total size of the transitional zone is mostly maintained by kinetic interlayer exchange processes at the leading displacement zone.

Once the asymptotic regime has established and the condition (5.20) become true, the process can be described by the macroscopic advection–dispersion Eq. 5.21 with asymptotic parameters u^* and D_L^* (Marle et al. 1967; Marinosehi et al. 1998).

5.2 Combined Influence of Vertical Advection and Diffusion in a Two-Layer Leaky System on Solute Transport

In leaky stratified (or multi-layer) groundwater systems contaminant transport in low-permeability (semipervious) beds can occur through both molecular diffusion and advection. Such leakage affects the rate and often the direction of migration in the semipervious bed and increases or decreases the groundwater flow discharge in the high-permeability layer (aquifer) and hence the horizontal advection velocity. At the same time, the leakage contributes to the dilution of solutions by the additional amounts of water entering the high-permeability layer. In the case of water withdrawal by wells, the vertical advection causes water with different chemistry to enter the aquifer from nearby hydrodynamic zones (Sect. 9.1).

5.2.1 Derivation of Analytical Solution

The system of transient solute transport and steady-state flow equations for a two-layer confined reservoir (Fig. 5.3) can be written as

$$\frac{\partial C_1}{\partial t} + \frac{\partial}{\partial x}(u_{x1}C_1) + \frac{W_s}{\phi_1} = 0, \quad (5.24)$$

$$\frac{\partial C_2}{\partial t} \pm u_{z2} \frac{\partial C_2}{\partial z} - D_m \frac{\partial^2 C_2}{\partial z^2} = 0, \quad (5.25)$$

$$\frac{\partial q_{x1}}{\partial x} \pm \frac{q_{z2}}{m_1} = 0; \quad (5.25a)$$

here, subscripts 1 and 2 refer to the aquifer and semipervious bed, respectively; W_s is the specific rate of interlayer exchange, defined as

$$W_s = -\frac{\phi_2 D_m}{m_1} \frac{\partial C_2}{\partial z} \Big|_{z=0} \pm \frac{q_{z2}}{m_1} C_2 \Big|_{z=0}, \quad (5.25b)$$

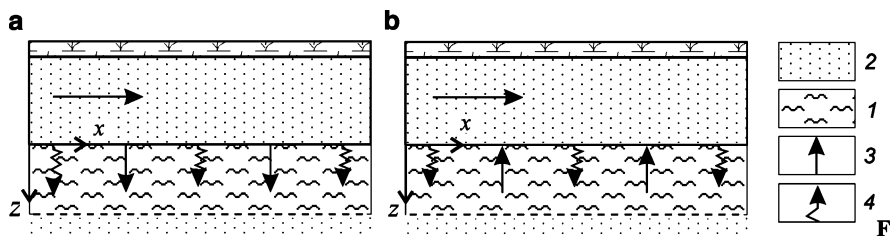


Fig. 5.3 Schematic diagrams of a two-layer system with crossflow in the semipervious bed. (a) The case of advection and diffusion in the same direction and (b) in opposite directions. (1) High-permeability layer (q_{x1} , m_1 , ϕ_1); (2) low-permeability layer (q_{z2} , D_m , m_2 , ϕ_2); (3), (4) advection and diffusion transport directions, respectively

where $|C_1 = C_2|_{z=0}$. Equation 5.24 describes solute balance in the aquifer; Eq. 5.25 describes diffusion transport accompanied by vertical convection (with a velocity of u_{z2}) in the semipervious bed; and Eq. 5.25a is flow continuity equation; the plus sign corresponds to the case when the diffusion and advection flows have the same directions (see Fig. 5.3a).

Upon substituting (5.25a) and (5.25b) into (5.24), the initial system of Eqs. 5.24–5.25b takes the more compact form

$$\frac{\partial C_1}{\partial t} + u_{x1} \frac{\partial C_1}{\partial x} - \frac{\phi_2 D_m}{\phi_1 m_1} \frac{\partial C_2}{\partial z} \Big|_{z=0} = 0, \quad (5.26)$$

$$\frac{\partial C_2}{\partial t} \pm u_{z2} \frac{\partial C_2}{\partial z} - D_m \frac{\partial^2 C_2}{\partial z^2} = 0, \quad (5.26a)$$

where $q_{x1} = -\left(\pm \frac{q_{z2}}{m_1} x\right) + q_{x1}^0$, q_{x1}^0 is the Darcy velocity in the inlet section of the aquifer.

Suppose that the characteristic time of the process t_0 is defined by formula (3.2), i.e.,

$$t_0 = \int_0^x \frac{\phi_1 dx}{q_{x1}} = \pm \frac{\phi_1}{b} \ln \left(\frac{a \pm bx}{a} \right), \quad (5.26b)$$

where $a = q_{x1}^0$, $b = -q_{z2}/m_1$.

Now taking the Laplace transform of both sides of Eqs. 5.26–5.26b yields the following system of ordinary differential equations (zero initial conditions):

$$p\tilde{C}_1 + \frac{d\tilde{C}_1}{dt_0} - \frac{\phi_2 D_m}{m_1 \phi_1} \frac{d\tilde{C}_2}{dz} \Big|_{z=0} = 0, \quad (5.26c)$$

$$p\tilde{C}_2 \pm u_{z2} \frac{d\tilde{C}_2}{dz} - D_m \frac{d^2 \tilde{C}_2}{dz^2} = 0, \quad (5.26d)$$

The solution of the transport equation in low-permeability layer (5.26d) is well-known (see Sect. 1.3.3.2 and formula (1.112), where the constant $A = \tilde{C}_1$):

$$\tilde{C}_2 = \tilde{C}_1 \exp \left\{ \left[\pm \frac{u_{z2}}{2D_m} - \frac{u_{z2}}{2D_m} \sqrt{1 + \frac{4D_m}{u_{z2}^2} p} \right] z \right\}. \quad (5.26e)$$

This allows us to find the derivative $dC_2/dz|_{z=0}$. Its substituting into (5.26c) yields:

$$\frac{d\tilde{C}_1}{dt_0} = - \left\{ p - \frac{\phi_2 D_m}{m_1 \phi_1} \left[\pm \frac{u_{z2}}{2D_m} - \frac{u_{z2}}{2D_m} \sqrt{1 + \frac{4D_m}{u_{z2}^2} p} \right] \right\} \tilde{C}_1. \quad (5.26f)$$

Integrating (5.26f) under the condition $C(t_0 = 0) = C_0$ yields the solution, which can be represented as

$$\tilde{C}_1 = \frac{C_0}{p} \exp \left[\pm \frac{P}{2} - \frac{P}{2} \sqrt{1 + \frac{4T_0}{P} p} \right] \exp(-pt_0), \quad (5.27)$$

where $P = u_{z2} \phi_2 t_0 / m_1 \phi_1$, $T_0 = D_m \phi_2 t_0 / u_{z2} m_1 \phi_1$.

Note that in this case, the product of the first two terms formally corresponds to the solution of the basic problem in Laplace transforms (1.113) provided that diffusion and advection in the low-permeability layer have the same direction. Otherwise, the same result can be obtained by multiplying the right and left parts of (5.27) by $\exp(P)$, whence we have

$$\tilde{C}_1^- = e^{-P} \tilde{C}_1^+. \quad (5.27a)$$

In accordance with the shift theorem, the exponential factor causes a shift in the current time by t_0 . Therefore, the inversion of function $\tilde{C}_1(p)$ at different directions of flow velocity in the low-permeability layer yields the following solution of the problem:

$$\tilde{C}_1^+ = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{1-T}{2\sqrt{T/P}} \right) + e^P \operatorname{erfc} \left(\frac{1+T}{2\sqrt{T/P}} \right) \right], \quad (5.28)$$

$$\tilde{C}_1^- = \frac{1}{2} \left[e^{-P} \operatorname{erfc} \left(\frac{1-T}{2\sqrt{T/P}} \right) + \operatorname{erfc} \left(\frac{1+T}{2\sqrt{T/P}} \right) \right], \quad (5.29)$$

where

$$T = \frac{u_{z2} m_1 \phi_1}{\phi_2 D_m} \left(\frac{t - t_0}{t_0} \right). \quad (5.29a)$$

The solutions (5.28) and (5.29), plotted in Fig. 5.4, are applicable at $t \geq t_0$.

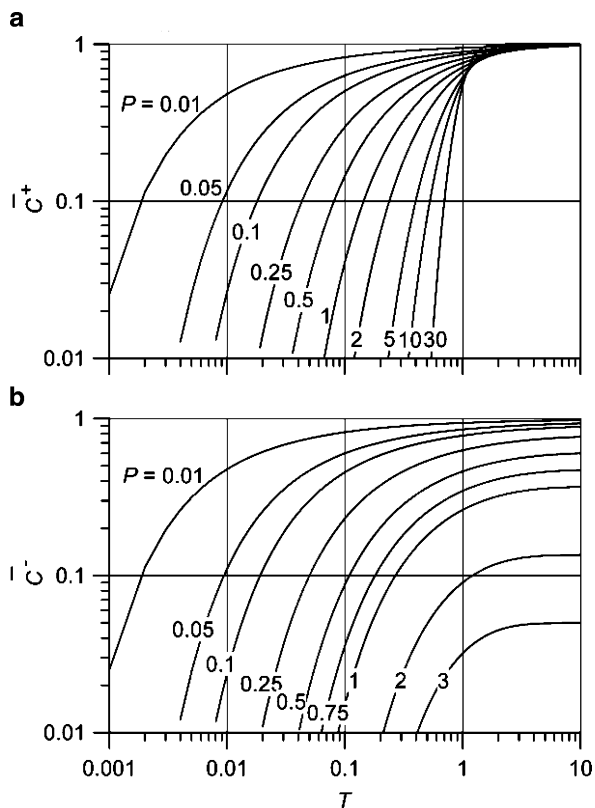


Fig. 5.4 Plots of concentration functions. (a) $\bar{C}^+ = f(T, P)$; (b) $\bar{C}^- = f(T, P)$

Define the derivative of the function (5.28):

$$\frac{d\bar{C}_1^+}{dT} = \frac{\sqrt{P}}{\sqrt{4\pi T^3}} \exp \left[-\frac{(1-T)^2}{4T/P} \right]. \quad (5.30)$$

It is obvious that

$$\frac{d\bar{C}_1^+}{dT} = \frac{d\bar{C}_1^+}{\beta d\bar{t}}, \quad \bar{t} = \frac{t}{t_0}, \quad \beta = \frac{u_{z2} m_1 \phi_1}{D_m \phi_2}. \quad (5.30a)$$

Whence, in accordance with (1.123), we can write the solution of the problem in the dimensionless form for the impulse input concentration signal (Dirac delta function, Eq. 1.117)

$$\bar{C}_{li}^+ = \frac{\beta \sqrt{P}}{\sqrt{4\pi T^3}} \exp \left[-\frac{(1-T)^2}{4T/P} \right]. \quad (5.31)$$

Accordingly

$$\bar{C}_{li}^- = e^{-P} \bar{C}_{li}^+. \quad (5.31a)$$

The solution (5.31) is a formal analogue of Houseworth's solution of migration problem in a single fissure in contact with porous medium (Houseworth 2006, formula 35). The incorporation into the model of advective exchange component between continuums was caused by the need to describe moisture migration in an incompletely saturated medium. The author also introduced the flow velocity component q_{x2} (in our notations).

When the leakage velocities are small, the solutions (5.28) and (5.29) tend to the limiting expression

$$\bar{C}_1^+ = \bar{C}_1^- = \operatorname{erfc} \left(\frac{1}{2\sqrt{T/P}} \right), \quad (5.32)$$

corresponding to the well-known Lauverier solution (5.13) (at $\tau/\eta^2 = T/P$, where η and τ are defined by Eqs. 5.11a).

Conversely, starting from the solutions for a linear flow given above, it can be shown that when $q_{z2x}/q_{x1}m_1 > 10$ (in the case of oppositely directed processes in the separating layer) and when $q_{z2x}/q_{x1}m_1 > 1$ (when the leakage and diffusion have the same direction), the diffusion exchange is of secondary importance. In the case of purely advective transport in the semipervious bed, when the main aquifer subject to contamination is recharged by the leakage of "clear" water from an adjacent aquifer, the solution (5.29) yields stationary asymptotics (see curves in Fig. 5.4b at large T):

$$\bar{C}_1^- = e^{-P}, \quad P = \ln \left(\frac{a+bx}{a} \right), \quad (5.33)$$

or

$$\bar{C}_1^- = \frac{1}{1 + q_{z2x}/q_{x1}^0 m_1}. \quad (5.33a)$$

Thus, the migration pattern in a two-layer system is determined, depending on leakage direction, either by the hydraulic mixing of waters with different chemistry (the transitional zone between the replacing and replaced solutions has a considerable length), or by the slowing of the propagation velocity of the concentration front because of the loss of a part of dissolved solute along with the solvent (the transitional zone in this case is not pronounced). Moreover, in the presence of head differential between aquifers, the solutions for purely diffusion schemes of interlayer exchange are justified only for small-length domains. This conclusion is especially significant for radial two-dimensional flows (see Sect. 9.1).

5.2.2 A Case Study: The Formation and Degradation of a Subsurface Iodine-Water Deposit (Paleohydrogeology Reconstruction)

The iodine deposit in question is a unique natural feature for which there are no analogues on the planet. A number of global geological processes as well as the climate change have played a considerable role in the formation of the deposit in relatively recent geological past. Nowadays we observe natural degradation of the deposit, – a process that can be described in the context of groundwater flow and solute transport at the regional scale.

5.2.2.1 Hydrogeological Background and Paleological Analysis

The iodine deposit confined to water bearing deposits of Padun suite, Vendian (V_{2pd}), is genetically related to the overlaying stratum ($m=30\text{--}70$ m) of Mikulian clay (m_{IIIImk}), occurring in the central part of Severodvinskaya depression (Arkhangel'sk province). The Padun aquifer lies at depths of 50–100 m from the surface, and its thickness reaches 100–120 m. The Padun rocks are represented by sandstones (60–80%) and aleurolites (20–30%), separated by argillite seams. Iodine concentration is nearly proportional to water mineralization (10–27 g/l) and varies from 10 to 30 mg/l (up to 40 mg/l in individual samples). Iodine waters are localized in the upper zone (about 40 m in thickness) of terrigenous deposits of Padun suite, Vendian. Commercial iodine reserves were explored in 1998–2004 in an area within the deposit (Bobrovskoe area) (Fig. 5.5).

The aquifer is mostly recharged from the overlying carbonate deposits (C_{2+3}) beyond the occurrence area of Mikulian clay, which is cut by the Northern Dvina River in the central part of the depression (Fig. 5.5). Groundwater flow discharges into its valley from northeast and southwest (Figs. 5.5 and 5.6). Its mean hydraulic gradient (J) varies around $2 \cdot 10^{-3}$ m/m.

Groundwater head increases with depth. The observed head differential between the Padun aquifer and Quaternary deposit aquifer in the flow discharge area is 3–5 m, thus creating possibility for ascending flow (leakage) in Mikulian clay. However, inverse relationship between heads can exist in the transit zone. The overall hydrodynamic picture is controversial.

The mean variation range of the hydraulic conductivity (k) of deposits of Padunian suite of Vendian is $0.5\text{--}1.5$ m day $^{-1}$, the mean porosity is about 25% (according to data of laboratory studies of rock samples). Pumping tests carried out during exploration of the Bobrovskoe area of the deposit in 2003–2004 showed that the dispersion of iodine-containing water all over the thickness of Padun deposits is hampered by a regionally occurring bed of low-permeability argillites, separating the upper part (about 30–40 m in thickness) of deposits with higher permeability from the lower parts of the same rock complex.

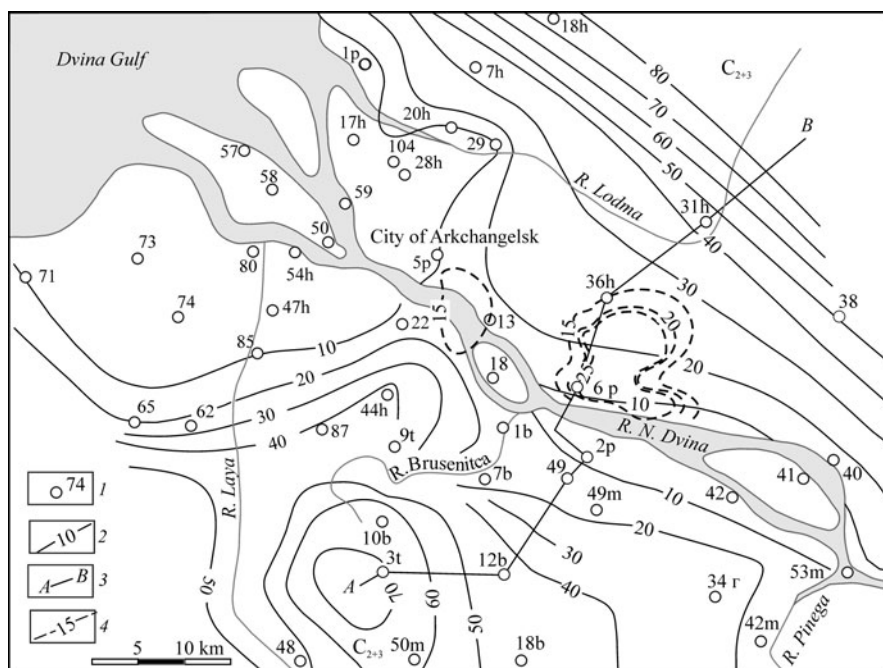


Fig. 5.5 Hydrogeological scheme of the Northern Dvina Depression. (1) Hydrogeological well, (2) hydroisohypses (meters above sea level), (3) section line (see Fig. 5.6), (4) iodine concentration isolines in Bobrovskoe area (mgL^{-1})

The interstitial water in Mikulian clay stratum is salt, its mineralization varying within 30 to 35 gL^{-1} ; water has chloride sodium chemistry close to that of seawater. Iodine concentration in interstitial water reaches 30 – 40 mgL^{-1} . Water mineralization tends to decrease from top to bottom.

The clay strata formed about 120 – 70 Ky ago in the period of Boreal sea transgression during Mikulian interglacial period in the White Sea coast. Originally, these were silts (with the porosity of about 60 – 80%) rich in organic remains of iodine-containing algae and plankton. High iodine concentrations are recorded now in silts in marginal shallow areas of seas and the ocean, which is due to the considerable enrichment of sediments by organic matter. This organic matter was the source of iodine in the pore solution of Mikulian clay. Nowadays, its porosity is estimated at about 40% and its density at 2.04 gcm^{-3} . Clay compaction, accompanied by squeezing of iodine-containing solutions into the underlying deposits of Padun suite of Vendian took place under the effect of clay's own weight and the weight of the Valdai glacier, overlying it 50 – 10 Ky ago.

A specific feature of the hydrogeological conditions in the region is the existence of a hydrochemical inversion in the upper 100 – 150 m part of the Vendian section, manifesting itself in a downward decrease in the mineralization of groundwater with chloride sodium and calcium–sodium composition. Iodine accumulation in the

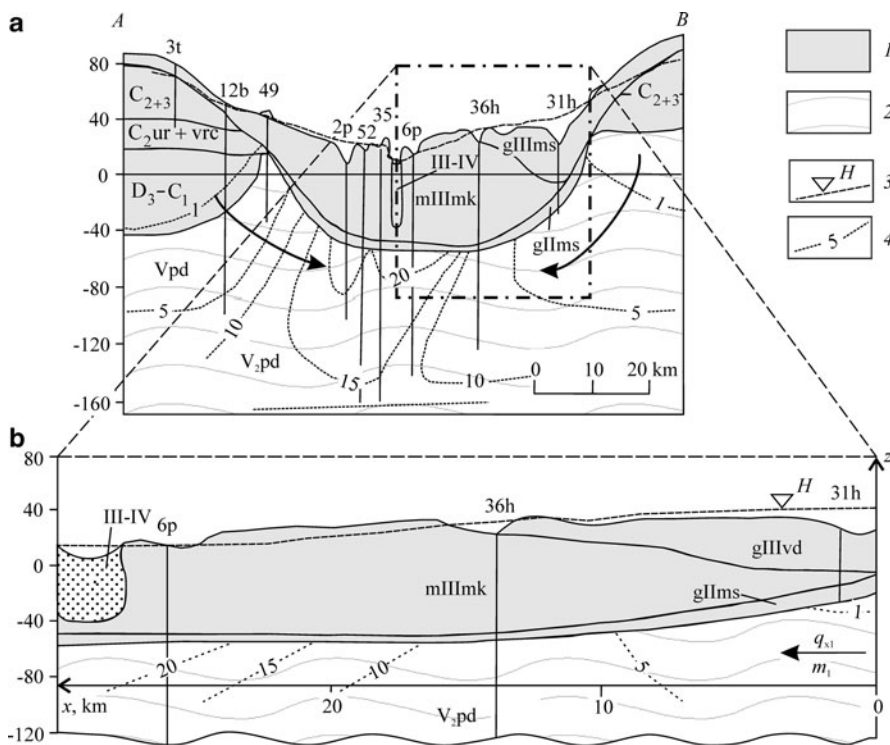


Fig. 5.6 (a) Regional hydrogeological section along A – B line in Fig. 5.5 and (b) a local window for profiling model. (1) Mikulian clay and terrigenous-carbonate rock of Devonian and Carboniferous overlying the Padun deposits; (2) Padun deposits; (3) groundwater level; (4) mineralization isoline (gL^{-1})

composition of water of marine genesis (with the mineralization of $30\text{--}35\text{ gL}^{-1}$), as it has been mentioned, was taking place mostly in the upper part of the Padun aquifer. The salinization of lower parts of the section, where current water mineralization does not exceed $10\text{--}12\text{ gL}^{-1}$ (the iodine content is no more than 5 mg L^{-1}), was hampered by the natural hydrodynamic stratification of the section (the presence of low-permeability argillite seams).

After the retreat of Valdai glacier, which had played an important role in the formation of iodine deposit, a period of destruction of this deposit started 10 Ky ago. This process is associated with the motion of fresh infiltration water that forms in the areas on the left and right sides of the Northern Dvina beyond the occurrence contour of Mikulian clays through salinized Padunskie rocks to the zone of their natural drainage. The effect of this process is the gradual replacement of iodine waters, resulting in stratal water freshening in zones adjacent to the recharge domain of the aquifer in deposits of Padun suite of Vendian. Iodine accumulations mostly occur in areas near the central part of the Northern Dvina depression. At the same time, higher iodine concentrations tend to persist in less permeable rock blocks, thus

confirming the hypothesis that the processes of natural destruction of the deposit are active. In this context, of some interest is the assessment of mechanisms hampering this process.

5.2.2.2 Quantitative Description of the Process

The major elements of process schematization are given in Fig. 5.6, showing an averaged section, which coincides with a flow line directed from the recharge area to the zone of groundwater discharge into the river valley. The section gives isolines of mineralization C . The appropriate values of $C = f(x)$ were used to calibrate the model of two-layer stratum with a lower layer composed of high-permeability Padun rocks, where horizontal advection predominates, and an upper layer composed of Mikulian clay, where molecular diffusion superimposed with ascending advection are major transport mechanisms.

The mean groundwater Darcy velocity along bedding is $q_{\text{aver}} = kJ = 2 \cdot 10^{-3} \text{ m/m} \cdot 1.25 \text{ m/d} = 2.5 \cdot 10^{-3} \text{ m/d} \approx 1 \text{ m/year}$. The thickness of the bed (the upper part of the section, where iodine is concentrated) is $m_1 = 40 \text{ m}$. The porosity values of Vendian and Quaternary deposits are $\phi_1 = 0.25$ and $\phi_2 = 0.4$, respectively. The initial water mineralization is $C_0 = 35 \text{ gL}^{-1}$ (seawater squeezed out of Mikulian clay). Fresh groundwater flow from the boundary $x = 0$ features the value of $C^0 = 1 \text{ gL}^{-1}$. The calculation period is $t = 10,000 \text{ year}$ (the freshening of Padun stratum is assumed to have started in the moment of completion of Valdai glaciation).

The calculations were based on the solution of migration problem (5.28)/(5.29) represented as

$$C^{\pm} = C_0 + (C_0 - C^0)\bar{C}^{\pm}, \quad (5.34)$$

where C^+ is water mineralization in the case of upward leakage, and C^- is that for downward leakage; in the former case, we have $t_0 = -(\phi_1 m_1 / q_{z2}) \ln(1 - q_{z2}x / m_1 q_{x1}^0)$; and in the latter case, $t_0 = (\phi_1 m_1 / q_{z2}) \ln(1 + q_{z2}x / m_1 q_{x1}^0)$.

The model (5.34) describes the freshening of Padun aquifer due to the displacement of iodine-containing mineralized water by regional flow of infiltration water. This model takes into account the diffusion of salt (and, accordingly, dissolved iodine) from the overlying Mikulian clay, a process that hampers the displacement. The ascending or descending water flow in the clay (resulting from head differential between the lower and upper aquifers), incorporated into the model, is a factor that slows down or accelerates mass transfer rate on the interface between solutions, as well as a factor that hampers interlayer mass exchange.

The first calculations by formula (5.34), carried out at $q_{z2} = 0$ (Lauverier solution), allowed us to fit parameter $\phi_2 D_m = 1.875 \cdot 10^{-2} = 5.125 \cdot 10^{-5} \text{ m}^2 \text{d}^{-1}$ to adequately describe the observed mineralization distributions $C(x)$ (Fig. 5.7a) in the profile in question (Fig. 5.6b) and yielded results that are very close to those obtained in diffusion laboratory experiments. One can see that the calculation results are sensitive to D_m variations, suggesting, in particular, the significant role of diffusion in the formation of the observed hydrogeochemical zonality of water in Padun

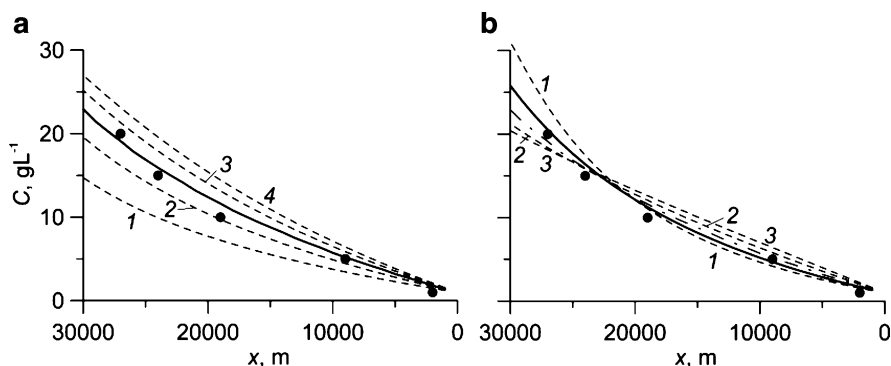


Fig. 5.7 Observed (dark circles) and calculated (curves) variations in groundwater TDS along a flowline. (a) variants of calculations at $q_{z2} = 0$: thick line is for $\phi_2 D_m = 1.875 \cdot 10^{-2} \text{ m}^2 \text{ yr}^{-1}$, dashed lines are for other values of parameter $\phi_2 D_m, \text{ m}^2 \text{ yr}^{-1}$: 1 - $6.25 \cdot 10^{-3}$, 2 - $1.25 \cdot 10^{-2}$, 3 - $2.5 \cdot 10^{-2}$, 4 - $3.125 \cdot 10^{-2}$; (b) variants of calculations with $q_{z2} \neq 0$: thick line $q_{z2} = 2 \cdot 10^{-4} \text{ m yr}^{-1}$, $\phi_2 D_m = 1.875 \cdot 10^{-2} \text{ m}^2 \text{ yr}^{-1}$, dashed lines are for other values of parameter $q_{z2}, \text{ m yr}^{-1}$: 1 - $(-4 \cdot 10^{-4})$, 2 - $(-2 \cdot 10^{-4})$, 3 - $(-4 \cdot 10^{-4})$, negative values mean the downward velocity direction, dash-and-dot line is for $\phi_2 D_m = 1.875 \cdot 10^{-2} \text{ m}^2 \text{ yr}^{-1}$, $q_{z2} = 0$

deposits. Otherwise, were it not for diffusion exchange, the migration velocities having the current values $u = q_{x1}/\phi_1 = 4 \text{ m yr}^{-1}$, the entire stratum would be filled with fresh infiltration water within the 10,000 years.

Next an attempt was made to improve fitting accuracy by incorporating into the model the vertical Darcy velocity in clays. As can be seen from Fig. 5.5b, specifying $q_{z2} = 2 \cdot 10^{-4} \text{ m yr}^{-1}$ (the velocity is directed vertically upward) somewhat improves the agreement between model results and field observations. With the observed values of vertical gradient $\Delta h/m_2 \approx (3 \div 5 \text{ m})/40 \text{ m} \approx 0.1$, the obtained value of q_{z2} corresponds to the hydraulic conductivity of Mikulian clay, k_2 , of about $5 \cdot 10^{-6} \text{ md}^{-1}$.

Thus, calculations show that the persistence of the iodine deposit is largely due to the diffusion exchange between the Padun aquifer and the overlying bed of iodine-containing Mikulian clays. The leakage is a factor of secondary importance. The latter conclusion is conformed by the Peclet number, whose low values imply the important role of diffusion mass exchange between the strata under consideration.

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Chapter 6

Analytical Models for Solute Transport in Saturated Fractured-Porous Media

Analysis and prediction of solute transport in fractured reservoirs is usually based on the dual porosity (mobile-immobile domain) concept. Matrix diffusion and equilibrium adsorption in the matrix influence dramatically on dissolved contaminants' retardation in the fracture-matrix system (Neretnieks 1980; Sudicky and Frind 1982; Mironenko and Rumynin 1986; Rasmuson and Neretnieks 1986a; Maloszewski and Zuber 1993; Zuber and Motyka 1994; Moench 1995; Callahan et al. 2000; Zhou et al. 2007). Matrix diffusion not only causes a delayed solute arrival time but also additional dispersion (due to rate-limited mass transfer between fractures and porous blocks) of the advanced solute front. On the other hand, fracture/matrix exchange kinetics causes the tailing effect that is a well-known limitation of pump-and-treat remediation systems wherein high concentrations of fracture domain contaminants are removed relatively quickly, followed by an asymptotic approach to a sustained period of much lower concentration related to the slow release of contamination from the matrix back to the fracture solution (Valocchi 1986; Cosler 2004). Matrix block porosity and size/length, fracture spacing, and matrix diffusivity along with the chemical identity of the contaminant are the parameters that most strongly govern the degree to which matrix diffusion prolongs the aquifer restoration process and control the length of time the aquifer will be decontaminated (Mutch et al. 1993).

Mobile-immobile domain formulation has been widely used for many years for solute transport analysis and typically refer to chemical or physical nonequilibrium systems defining the immobile phases as either a solid sorbed phase in contact with mobile water or immobile water in pore spaces (lenses of low permeability media, intra-aggregate porosity, dead-end pores, matrix porosity of fractured media) in contact with mobile water. Even highly heterogeneous aquifers with potentials for preferential pathways can create a system of immobile and mobile domains (Feehley et al. 2000). The theory of solute transport in the fractured media to be presented below therefore is of fundamental interest in view of the subsurface contaminant hydrology.

6.1 Governing Parameters and Conceptual Model Formulation

The dual porosity concept implies that the fluid flows in a system of continuous fractures of high permeability and low porosity that surround discontinuous matrix blocks of much lower permeability but higher porosity (where water movement is ignored). This suggests the well-known concept of the two basic mass transport mechanisms – a convective in fractures and a molecular diffusion in porous matrix; in some variants, solute hydrodynamic dispersion in flow-carrying fractures is taken into account, as well as sorption and decay. As a rule, the porosity contrast between matrix, ϕ_m , and fractures, ϕ , around one order of magnitude will be quite sufficient for the character of the transport of solutes, assimilated by pore blocks, to be completely determined (at the regional scale) by the dual porosity of the system.

The pore space in the matrix blocks represents a significant reservoir into (and out of) which solute can diffuse from (and into) the fractures. An indirect proof of the effect of matrix diffusion on mass transport in fractured rocks is the divergence between the breakthrough curves obtained in tracer experiments with chemicals featuring different molecular diffusion coefficients, D_m , in the porous matrix (Hu and Brusseau 1995; Callahan et al. 2000; Reimus et al. 2003). Guimerà and Carrera (2000) examining data from a number of tracer tests in fractured rock (with a Dirac input function) on a wide range of space and time scales found that the evidence for matrix diffusion can be the frequently observed apparent porosity grows as the square root of tracer peak arrival time.

6.1.1 Parameters and Topological Presentation of Fractured Rock Continuum

There are two modeling approaches for groundwater flow and transport through fractures or fracture networks. The first approach is the continuum approach where fluid flow and solute transport can be implicitly described in fractured media. The most popular is the *dual-continuum model*. In the dual-continuum approach, the aquifer is conceptualized as consisting of two overlapping domains (continua), a fracture domain, in which transport is dominated by advection, and a porous matrix domain in which transport is mostly by molecular diffusion. The exchange between the two domains is characterized by a mass transfer term (Black and Kipp 1983; Gerke and van Genuchten 1993a,b; Haggerty and Gorelick 1995; Carrera et al. 1998; Feehley et al. 2000; Harvey and Gorelick 2000; Kocabas and Islam 2000; Haggerty et al. 2004). The model and in particular an assumption on quasi-state regime (see Sect. 6.1.2.3) of water transfer between the fracture and matrix domains was proposed initially for studying the exploitation of fractured groundwater and petroleum reservoirs (Barenblatt et al. 1960; Warren and Root 1963; Barenblatt et al. 1990).

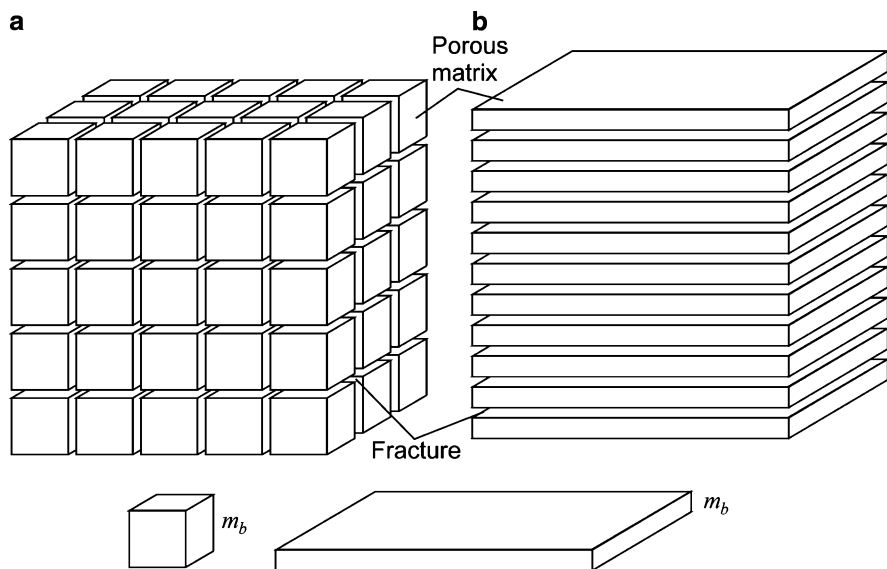


Fig. 6.1 A schematic representation of fractured rock continuum (systems with a periodic cell structure): (a) matrix blocks of cubic shape, (b) matrix blocks of rectangular slab shape

The idealistic concepts assuming the fragmentation of a rock massif by fracture systems result in models of media with a periodic cell structure (Fig. 6.1). Accordingly, the characteristics of transport rate in fractures will be Darcy velocity, $\mathbf{q}$, and the effective fracture porosity, ϕ , while the transport in the porous matrix will be characterized by the pore diffusion coefficient, D_m , the porosity, ϕ_m (the volume of voids per unit volume of matrix), and the averaged geometric characteristic relating to the average size of matrix blocks, m_b (Fig. 6.1a), and/or their specific surface, S_b . With fractured rocks described in such a manner, it was found convenient to take into account their dual porosity nature in the framework of *asymptotic models* to be chosen depending on the specific features of transport regime in the blocks and related to the scale of process analysis as a whole (Mironenko and Rumynin 1986; Carrera et al. 1998).

The second approach focuses on flow and mass transport in one or more individual fractures and is called the *discrete approach* (Berkowitz 2002; Reeves et al. 2008a,b). Numerical and coupled numerical-and-analytical modeling technique becomes the major tool for studying solute transport in fracture networks. Such process can be simulated in two ways (Novakowski and Sudicky 2007): using (1) particle tracing, and (2) direct solution of the governing equations for solute transport.

Widely used in practice were models describing solute migration in individual fractures (Neretnieks 1980; Grisak and Pickens 1981; Tang et al. 1981; Barker 1982; Neretnieks 1983; Novakowski et al. 1985; Maloszewski and Zuber 1990, 1999; Novakowski and Lapcevic 1994; Callahan et al. 2000; Bodin et al. 2003; West et al.

2004). When a fracture is not filled with disperse material, its storage capacity is determined by its aperture (the mean distance between its walls, $2b_f$), and the advection, by the specific flow discharge, $Q_f = 2b_f u$. The distance between parallel fractures $m_b = 2a_m$ (Fig. 6.1b), along with molecular pore diffusion coefficient and porosity, determine the filling rate of the porous matrix by the solute during long-time migration. This rate, however, can be reduced by the effect of films on fracture wall surface, which are represented by oxides and hydroxides of various metals and secondary minerals. The effect of such additional diffusion “resistance” may require more complicated migration models (Wallach and Parlange 2000).

The mathematical description of migration in a fractured-porous aquifer is based on Eq. 1.25, where the mass transfer rate function (or sink/source function), W_s , presents diffusive mass flux across the fracture/porous matrix interface. This equation with $W_f = 0$ in the case of migration of nonreactive and stable components is conveniently expressed in the following generalized form

$$\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C - \nabla \cdot (\mathbf{D} \cdot \nabla C) + \sigma W_{sr} = 0, \quad (6.1)$$

where $W_{sr} = W_s/\phi_m$ is the reduced transfer rate function corresponding to net solute exchange rate per unit volume of matrix pore space per unit time [$\text{ML}^{-3}\text{T}^{-1}$]; we also introduce here a porosity (capacity) ratio, *capacity coefficient*, $\sigma = \phi_m/\phi$. A mathematical formalization of the solute transport process accompanied by adsorption and contaminant decay is presented in Sect. 6.4.

6.1.2 Mass Transfer Functions

6.1.2.1 A General Form of Mass Transfer Rate Function

Mass transfer rate can be described by a convolution product of concentration (or concentration time derivative) in the fracture domain and a memory function in one of the forms of *Duhamel* integral

$$W_{sr} = \int_0^t \frac{\partial C}{\partial t}(t-\tau) g(\tau) d\tau = \frac{\partial}{\partial t} \int_0^t C(t-\tau) g(\tau) d\tau, \quad (6.2a)$$

$$W_{sr} = \int_0^t \frac{\partial C(\tau)}{\partial \tau} g(t-\tau) d\tau = \frac{\partial}{\partial t} \int_0^t C(\tau) g(t-\tau) d\tau; \quad (6.2b)$$

Representation (6.2) is valid for zero initial conditions, $C(+0) = 0$, $g(+0) = 0$; here $g(t) = \varphi(t)/\phi_m$ is a *memory function*; $\varphi(t)$ is a function, accounting for molecular diffusion discharge of solute from fractures into the pore matrix with constant unit concentration on the surface of the fracture [T^{-1}]; τ is a variable of integration [T]. Functions $g(t)$ and $\varphi(t)$ depend, in addition to time, on transfer coefficient in

the matrix and its geometry. With the choice of appropriate memory function, the model (6.2) can reproduce different types and regimes of mass transfer between the two domains.

Convolution integrals for a source term W_{sr} (6.2) in Laplace images (Sect. 6.1.3.3) have the general form:

$$\tilde{W}_{sr} = p\tilde{C}(p)\tilde{g}(p), \quad (6.3)$$

where $\tilde{C}(p)$ and $\tilde{g}(p)$ are images of functions $C(t)$ and $g(t)$.

The farther description of the process is conveniently related to the *space–time scale* of its analysis by determining asymptotic expressions for function $g(t)$ and, accordingly, W_{sr} (W_s). In this context, let us consider the following alternative approaches.

6.1.2.2 Geometry-Based Diffusion Model

For geometrically well-defined fracture systems, where diffusion takes place within uniformly sized blocks of basic geometric shape, one of the dependent variables can be associated with a *local concentration* in the matrix block, $C_a = C_a(\rho, t)$; this concentration is a function of the space coordinate ρ within the block and time t . Then the mass transfer of solute per unit area at the fracture and matrix interface is given by the Fick's law:

$$W_s = \phi_m W_{sr} = -S_b \phi_m D_m \left\langle \frac{\partial C_a}{\partial \rho} \right\rangle_{\rho \in S}, \quad (6.4)$$

where ρ is the internal normal to the external surface of the block; D_m is the pore diffusion coefficient; S_b is the specific surface of the matrix (matrix surface area, ω_b , per aquifer unit volume, V_b), $S_b = \omega_b/V_b$ [L^{-1}]. For a periodic system represented by blocks of cubic shape, we have $S_b = 6/m_b$ (Fig. 6.1a), and for blocks with a shape of rectangular slabs, $S_b = 2/m_b$ (Fig. 6.1b). It is assumed that the whole fracture surface is open to flow. Some studies however are based upon an alternative concept according to which the fracture surface is partially open to flow such that flow is “channelized” (Uchida et al. 2009).

For porous blocks of basic geometric shapes, the diffusion equation has a generalized one-dimensional representation (Crank 1975; Haggerty and Gorelick 1995):

$$\frac{\partial C_a}{\partial t} = \frac{D_m}{\rho^{(v-1)}} \frac{\partial}{\partial \rho} \left(\rho^{(v-1)} \frac{\partial C_a}{\partial \rho} \right), \quad (6.5)$$

where the superscripts $v = 1, 2, 3$ correspond to blocks of *rectangular-slab*, *cylindrical*, and *spherical* shapes. Thus, solutions, obtained for diffusion in porous blocks in shape of rectangular slabs can be used for describing transport process in a system of parallel fractures (Fig. 6.1b). Spherical inclusion of diameter $2a_m$ embedded in a

cubic matrix of length m_b would describe process in a uniformly (in 3D directions) fractured system (Fig. 6.1 a).

The boundary conditions for Eq. 6.5:

$$\frac{\partial C_a}{\partial \rho} = 0 \text{ in the center of the block and } C_a = C \text{ on block surface;} \quad (6.5a)$$

here C is solute concentration in the solution filling fractures.

The solutions of Eq. 6.5 at constant (unit, $\bar{C}_a = \bar{C} = 1$) concentration on the external surface of the block are well-known. For example, the dimensionless concentration of a solute in a porous block of rectangular shape is as follows (Carslaw and Jaeger 1959; Crank 1975):

$$\bar{C}_a(\bar{\rho}, \tau) = 1 - \sum_{k=1}^{\infty} \frac{2}{\alpha_k} \exp(-\alpha_k^2 \tau) \sin(\alpha_k \bar{\rho}), \quad (6.6)$$

where $\bar{\rho} = \rho/a_m$, $\alpha_k = (2k-1)\pi/2$, $\tau = D_m t/a_m^2$, $a_m = m_b/2$; $\bar{\rho} = 0$ ($\bar{C}_a = 1$) corresponds to the slab surface, $\bar{\rho} = 1$ ($\partial \bar{C}_a / \partial \bar{\rho} = 0$) is the center of the slab.

Then, according to the definition given in Sect. 6.1.2.1, the expression for memory function, $g(t)$, can be presented in the form:

$$g(t) = -\frac{S_b D_m}{a_m} \Gamma(\tau), \quad (6.7)$$

$$\Gamma(\tau) = \left\langle \frac{\partial \bar{C}_a}{\partial \bar{\rho}} \right\rangle_{\bar{\rho}=0} = -2 \sum_{k=1}^{\infty} \exp(-\alpha_k^2 \tau), \quad \tau = \frac{D_m t}{a_m^2}. \quad (6.8)$$

The solutions of diffusion equations in blocks of cylindrical and spherical shapes yield similar expression for the dimensionless concentration gradient at the fracture/matrix interface, $\Gamma(\tau)$; therefore, in the generalized form, we can write (Carrera et al. 1998):

$$\Gamma(\tau) = -\sum_{k=1}^{\infty} \varepsilon_k \exp(-\alpha_k^2 \tau), \quad (6.9)$$

where $\varepsilon_k = 2, 1/2$, and $2/3$ for a slab, cylinder, and sphere, respectively; the parameter α_k also has individual representations, depending on the geometric features of the porous matrix, $\alpha_k = (2k-1)\pi/2$, $u_k/2$ [the roots of equation $J_0(u_k) = 0$] and $k\pi/3$.

At *early times*, $\tau \ll 1$, function $\Gamma(\tau)$ (6.9) has the asymptotics: $\Gamma(\tau) = -(\pi\tau)^{-1/2}$. From here, considering (6.7), we have

$$g(t) = \sqrt{\frac{\lambda_m}{\pi t}}, \quad (6.10)$$

where

$$\lambda_m = S_b^2 D_m \quad (6.11)$$

is a combined mass transfer (exchange) coefficient, with dimensions of $[T^{-1}]$. It can be seen that the block size, which determines its specific surface, S_b , is indirectly involved in the expression for the memory function. Physically, this can be attributed to the fact that at early times, the diffusion of components from block surface toward its center proceeds along trajectories that have only weak effect on one another (actually, solute diffusion is plane-parallel).

The model (6.2)/(6.10) where diffusion is assumed to occur into an infinite matrix volume and a matrix block length was referred to as *unlimited matrix diffusion model*: its application is justified while only the porous matrix zone immediately adjacent to fractures is affected by molecular diffusion.

6.1.2.3 First-Order Approximation of Matrix Diffusion

At relatively *late times*, when the mass transport embraces a considerable portion of block pore space, the solute mass transfer rate, W_s can be related to average concentrations C and C_m under quasi-steady conditions as (Black and Kipp 1983; Mironenko and Rumynin 1986, 1998; Haggerty and Gorelick 1995; Haggerty et al. 2004)

$$W_{sr} = \frac{W_s}{\phi_m} = \frac{\partial C_m}{\partial t} = \alpha_m(C - C_m). \quad (6.12)$$

This model is a formally adopted first-order approximation of matrix diffusion and therefore can be named the *first-order transport model* (Gerke and van Genuchten 1993a, b; Haggerty and Gorelick 1995; Haggerty et al. 2004). Therefore

$$\alpha_m = D_m S_b / l_e \quad (6.13)$$

is the first-order mass transfer coefficient that has inverse-time unit $[T^{-1}]$; $l_e < a_m$ is a characteristic (effective) diffusion path length inside the porous block. As model (6.12) utilizes an *average concentration*, C_m , it is also frequently named *lumped capacitance model*. Formally, an integral representation of function C_m can be obtained in the context of geometry-based diffusion model:

$$C_m = \frac{v}{a_m^v} \int_0^{a_m} \eta^{(v-1)} C_a(\eta) d\eta, \quad (6.14)$$

where C_a is determined from the solution of the diffusion Eq. 6.5, a_m is slab half-thickness or the radius of the generatrix of the cylinder/sphere surface.

A variety of techniques have been used to derive expressions for the first-order mass transfer coefficient, α_m (van Genuchten and Dalton 1986; Gerke and van Genuchten 1993a, b, 1996; Mathias 2005), including numerical modeling approach (Mironenko and Rumynin 1986), Laplace transform comparison (Rasmuson and Neretnieks 1986a, b; Moench 1995), and moment analysis

(Parker and Valocchi 1986; Valocchi 1990; Govindaraju and Das 2007). These studies have demonstrated that the first-order mass transfer coefficient is of the general form (Gerke and van Genuchten 1993a, b, 1996)

$$\alpha_m \approx \frac{\omega D_m}{a_m^2}, \quad (6.15)$$

where ω is a shape factor that depends on geometry; $\omega = 3 - 15$, where the minimal value corresponds to rectangular slabs (Fig. 6.1b) and the maximal, to spheres that can be associated with porous blocks of isometric shape (Fig. 6.1a). From formal analysis of (6.13) and (6.15), it follows that the effective transport distance in the blocks is $l_e = a_m/3$ and $l_e = a_m/5$ for rectangular slabs and spheres, respectively. Somewhat different interval was obtained from Laplace transform comparison approach (Haggerty and Gorelick 1995): $\omega = \pi^2/4 - \pi^2$. Additional discussion about how the effective coefficient α_m can vary depending on transport process formalization is presented in a paper by Chastanet and Wood (2008).

As a very rough approximation for preliminary estimates of migration in an aquifer consisting of blocks with approximately isometric shape, we can assume

$$\alpha_m \approx S_b^2 D_m \approx \lambda_m, \quad (6.15a)$$

which enables the use of coefficients λ_m , obtained in short-time tracer experiments, for predicting long-term solute migration.

Basing on (6.12), we can transform the expression for reduced mass transfer rate, W_{sr} , to a more general integral form (6.2) with function $g(t)$ defined as

$$g(t) = \alpha_m e^{-\alpha_m t}. \quad (6.16)$$

The characteristic residence time (mass transfer time) in the matrix blocks, t_m [T], is (Haggerty et al. 2004)

$$t_m = \int_0^\infty \tau g(\tau) d\tau = \frac{1}{\alpha_m}. \quad (6.16a)$$

Adaptation of the first-order mass transfer model for describing initial stages of solute transport in fractured porous media (spherical geometry) results in an explicit closed-form expression for the time-varying effective mass transfer coefficient, $\alpha_m(t)$, as follows (Chastanet and Wood 2008)

$$\alpha_m(t) = 15 \frac{D_m}{a_m^2} + 6 \frac{D_m}{a_m^2} \sum_{k=1}^{\infty} \exp\left(-\frac{\varepsilon_k^2 D_m}{a_m^2} t\right), \quad (6.17)$$

where ε_k s are the positive (nonzero) roots of equation $\text{th}\varepsilon_k = 3\varepsilon_k/(3 - \varepsilon_k^2)$ (Crank 1975). Basing on (6.17), it can be shown that coefficient $\alpha_m(t)$ has two asymptotics, leading to the memory functions obtained before: at $t \rightarrow 0$ $g(\tau) = \alpha_m \gamma / \sqrt{\pi \tau} = \sqrt{\lambda_m / \pi t}$; at $t \rightarrow \infty$ $g(\tau) = \alpha_m \exp(-\tau)$; here $\tau = \alpha_m t$, $\gamma = \sqrt{9/15}$.

6.1.2.4 Multi-Rate Matrix Diffusion

The models for mass transfer functions and coefficients given above do not take into account the statistical character of the fractured media. Indeed, variations in matrix block size/length and, consequently, in mass transfer coefficient, α_m , may result in additional complexification of the concentration distributions. For example, for a pulse injection, this implies that the mass transfer processes often generate heavily tailing breakthrough curves (Feehley et al. 2000; Cosler 2004; McKenna and Selroos 2004; Luo et al. 2008; Gouze et al. 2009), and therefore it often happens that the models with the average transfer coefficient fail to capture the real nature of the dispersion in natural systems.

Fortunately, the considered above classical first-order single-rate model (6.12) can be extended to build more general multi-rate mass transfer functions and equations. The multi-rate model differs from the first-order and geometry-based diffusion models in that several rates of mass transfer (within the representative volume) can be simulated simultaneously (Haggerty and Gorelick 1995; Gwo et al. 1998; Cosler 2004; Benson and Meerschaert 2009). In such model the first-order coefficient can be represented as a statistical distribution, having a probability density function, $b(\alpha_m)$, with a mean and a variance. Then the multi-rate mass transfer is described by the following memory function (Haggerty et al. 2000; McKenna and Selroos 2004; Luo et al. 2008)

$$g(t) = \int_0^{\infty} \alpha_m b(\alpha_m) e^{-\alpha_m t} d\alpha_m. \quad (6.18)$$

Thus, for a set of matrix blocks with a *continuously distributed* set of sizes/lengths, a lognormally distributed variable α_m , $b(\alpha_m)$ [T], is defined as

$$b(\alpha_m) = \frac{1}{\alpha_m \sigma_\alpha \sqrt{2\pi}} \exp \left\{ -\frac{[\ln(\alpha_m/m)]^2}{2\sigma_\alpha^2} \right\}, \quad (6.18a)$$

where m is the median mass transfer rate; σ_α is the standard deviation of $\ln \alpha_m$.

For a set of matrix blocks with *discretely distributed* set of sizes/lengths, a formulation for the mass transfer function can be obtained from (Haggerty and Gorelick 1995; Gwo et al. 1998)

$$W_{sr} = \sum_i^N \sigma_i \frac{\partial C_{mi}}{\partial t}, \quad (6.18b)$$

$$\frac{\partial C_{mi}}{\partial t} = \alpha_{mi}(C - C_{mi}), \quad i = 1, 2, \dots, N \quad (6.18c)$$

where $\sigma_i = \phi_{mi}/\phi$; α_{mi} is the first-order mass transfer coefficient for the i -th block; N is the amount of matrix blocks in a block set with defined size/length.

In comparison with mass transfer models discussed above, the multi-rate model fits better for simulating the tailing effect wherein contaminant diffusion from porous matrix with very slow mass transfer rates causes fracture concentrations (and mass removal rates) to be much lower than concentrations predicted by classical single-rate or single-porosity models (Cosler 2004).

When dealing with real hydrogeological systems, one should also take into account the superposition of macrodispersion effects caused by the flow heterogeneity (due to the spatial variations in hydraulic conductivity) of the fractured-porous formations (Sect. 6.3).

Below we consider approximate solutions that can be represented in a closed analytical form.

6.1.3 Basic Analytical Solutions (for Asymptotic Models)

Such solutions include solutions of Eq. 6.1 written for the case of one-dimensional solute transport in the form

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} - D_L \frac{\partial^2 C}{\partial x^2} + \sigma \int_0^t \frac{\partial C(t-\tau)}{\partial t} g(\tau) d\tau = 0, \quad g(\tau) = \frac{\varphi(\tau)}{\phi_m}, \quad (6.19)$$

where $u = q/\phi$ is the real fluid velocity in the fracture network, D_L is the coefficient of longitudinal dispersion; $g(\tau)$ is a transformed memory function; $\sigma = \phi_m/\phi$.

Equation 6.19 describes a transient linear mass transfer system subject to advection and dispersion (Luo et al. 2008). The source term describing the concentration change within the immobile domain is determined by a linear convolution, in which the concentration in the mobile domain is the input function and the memory function $g(t)$ is the unit impulse response function. By specifying particular parametric models, $g(t)$, we can reproduce the different regimes of the mass exchange between the fracture and porous matrix domains of different topology. For the multi-rate mass transfer, function $g(t)$ is determined by (6.18).

6.1.3.1 General Solution in Laplace Transforms

The Laplace transform of (6.19) is

$$\left(\tilde{C} - \frac{C^0}{p} \right) p + u \frac{d\tilde{C}}{dx} - D_L \frac{d^2 \tilde{C}}{dx^2} + \left(\tilde{C} - \frac{C^0}{p} \right) \sigma \tilde{g}(p) = 0, \quad (6.20)$$

where C^0 is the initial concentration; $\tilde{g}(p)$ is the Laplace transform of the memory function. Combining the first and last terms in (6.20), we obtain

$$\chi \left(\tilde{C} - \frac{C^0}{p} \right) + u \frac{d\tilde{C}}{dx} - D_L \frac{d^2 \tilde{C}}{dx^2} = 0, \quad (6.21)$$

where function $\chi = \chi(p)$ has two main representations:

$$\chi = p + \sigma \tilde{g}(p), \quad \text{where } \tilde{g}(p) = \sqrt{\lambda_m p}, \quad (6.21a)$$

$$\chi = p + \sigma \tilde{g}(p), \quad \text{where } \tilde{g}(p) = \frac{\alpha_m p}{(p + \alpha_m)} \quad (6.21b)$$

for unlimited matrix diffusion and lumped capacitance models, respectively.

The ordinary differential Eq. 6.21 with *constant* boundary $C(t, 0) = C_0$ and initial conditions $C(0, t) = 0$ has the following solution (see Sect. 1.3.3):

$$\tilde{C} = \frac{C_0}{p} \exp\left(\frac{ux}{2D_L}\right) \exp\left(-\frac{ux}{2D_L} \sqrt{1 + \frac{4D_L}{u^2} \chi}\right). \quad (6.22)$$

In accordance with (1.121) we have for an *impulse* input signal in the form of Dirac delta function:

$$\tilde{C}_i = \frac{M}{qS} \exp\left(\frac{ux}{2D_L}\right) \exp\left(-\frac{ux}{2D_L} \sqrt{1 + \frac{4D_L}{u^2} \chi}\right). \quad (6.22a)$$

With a piston-like motion of solute in the aquifer ($D_L \rightarrow 0$), the solutions (6.22) and (6.22a) can be simplified:

$$\tilde{C} = \frac{C_0}{p} \exp(-\chi t_0), \quad (6.23)$$

$$\tilde{C}_i = \frac{M}{qS} \exp(-\chi t_0). \quad (6.23a)$$

Taking into account that for many practical applications the dispersivity becomes secondary in the dual domain mass transfer models, it is these solutions that are of most interest in the context of assessing the effect of dual porosity of the medium on the character of migration process as a whole.

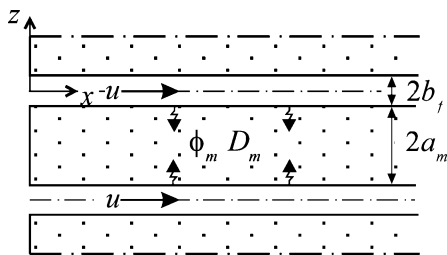
6.1.3.2 A Solution for Unlimited Matrix Diffusion Case

For the function image (6.23) with parameter χ , determined by (6.21a) (*diffusion model*), we have a tabulated original (Bateman and Erdelyi 1954; Doetsch 1967, 1974), allowing the solution to be written as (Mironenko and Rumynin 1986)

$$\bar{C} = \operatorname{erfc}\left(\frac{\eta}{2\sqrt{\tau}}\right), \quad \tau \geq 0, \quad (6.24)$$

$$\eta = \sigma \lambda_m t_0, \quad \tau = \lambda_m (t - t_0), \quad t_0 = \frac{x}{u}. \quad (6.24a)$$

Fig. 6.2 Conceptual scheme of solute transport in a system of parallel fractures



Formula (6.24) is an analogue of *Lauverier solution* (5.13) for a two-layer bed.

When the scale of migration in fracture-porous rocks is limited, there are reasons to use models describing *transport in individual fractures* (Fig. 6.2). In this case, by analogy with a two-layer reservoir (see Sect. 5.1.2) and, assuming that advection takes place in fractures with constant aperture, $2b_f$, conventionally isolated from one another, we represent the initial mass balance equation as

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} - D_L \frac{\partial^2 C}{\partial x^2} - \frac{D_m \phi_m}{b_f} \left(\frac{\partial C_a}{\partial z} \right)_{z=b_f} = 0. \quad (6.25)$$

The matrix diffusion equation has the form of (6.5) ($v = 1$, $\rho \equiv z$), and the boundary conditions are

$$C_a(z = b_f, t) = C, \quad \partial C_a(z = a_m, t) / \partial z = 0; \quad (6.25a)$$

here u is flow velocity in fractures, b_f fracture half-width, a_m is half-thickness of the slab associated with the porous block.

The solution of the problem in Laplace transforms (Barker 1982; Maloszewski and Zuber 1983; Mathias 2005) is also given by formulas (6.22), (6.22) and (6.23), (6.23) with

$$\chi = p \left[1 + \frac{\sigma}{m} \operatorname{th} m \right], \quad m^2 = \frac{a_m^2 p}{D_m}, \quad \sigma = \frac{a_m \phi_m}{b_f}, \quad t_0 = \frac{x}{u}. \quad (6.25b)$$

If the fracture is filled by disperse material with porosity ϕ , then $\sigma = a_m \phi_m / b_f \phi$, $u = q / \phi$.

The physical similarity of the process with migration in a two-layer reservoir (see 5.1.2), and the formal analogy of solutions in Laplace transforms (5.10), (5.10b) and (6.23), (6.25) allow us to describe mass transfer in the fracture by solution (5.11), where

$$\eta = \sigma \lambda'_m t_0, \quad \tau = \lambda'_m (t - t_0), \quad \lambda'_m = D_m / a_m^2. \quad (6.25c)$$

When time is small (the values of complex variable p are large), we have $m \approx 1$ in the expression for function χ ; therefore, $\chi \approx p + \sqrt{D_m \phi_m^2 p / b_f}$. This allows the solution to be written as

$$\bar{C} = \operatorname{erfc} \left(\frac{t_0}{2} \sqrt{\frac{B_m}{t - t_0}} \right), \quad (6.26)$$

similar to (6.24); here $B_m = D_m \phi_m^2 / b_f^2$. The representation of solution in the form of (6.26) is justified in the analysis of processes in weakly disintegrated (large-block) fractured rocks, when the transportation of a solute (e.g., an indicator during rock tests) over large distance occurs through one or several subhorizontal fractures.

To find the solution, reflecting the response of an aquifer to an *impulse* signal (with the assumption that the storage capacity of pore blocks is infinite and the propagation of solute front in fractures is piston-like), we can use formula (1.123), implying the differentiation of (6.24) or (6.26), yielding the following relationship:

$$\bar{C}_i = \frac{C_i \phi S x}{M} = \frac{\sqrt{\bar{\lambda}}}{\sqrt{4\pi(\bar{t} - 1)^3}} \exp \left[-\frac{\bar{\lambda}}{4(\bar{t} - 1)} \right], \bar{t} = \frac{t}{t_0} = \frac{qt}{x\phi}, \bar{\lambda} = B_m t_0, \quad (6.27)$$

here M is injected solute mass [M]; S is flow cross section [L²]; $B_m = \sigma^2 \lambda_m$ is a uniformly fractured bed with averaged mass exchange coefficient λ_m (6.11); $B_m = D_m \phi_m^2 / b_f^2$ is an individual fracture with an aperture of $2b_f$ in a porous massif. Formula (6.27) or more general solutions, taking into account dispersion in fractures can be obtained by some other methods of solving the boundary-value problem (Neretnieks 1983; Maloszewski and Zuber 1985; Zhou et al. 2007). It is noteworthy that solution (6.27) is similar to solution (5.31). The latter was obtained for a two-layer system, where diffusion interlayer exchange was complicated by advection. The solution for advection in a radial flow has the same structure, see formula (8.55) below.

In the case of a bed represented by blocks of mostly cubical configuration, the calculation scheme with infinite capacitance is valid while (Mironenko and Rumynin 1986)

$$\tau < 0.3 - 0.5. \quad (6.28)$$

6.1.3.3 A Solution of Equation for First-Order Kinetics

Now represent function (6.23), which at χ defined by (6.21b) corresponds to problem solution for first-order *single-rate* fracture-matrix exchange kinetics (*lumped capacitance model*), as

$$\tilde{C}(\eta, s) = \frac{1}{s} \exp \left(-\frac{\eta s}{s + 1} \right), \quad (6.29)$$

where $\tilde{C}(\eta, s) = \int_0^\infty \bar{C}(\eta, \tau) \exp(-s\tau) d\tau$, s is transformation parameter of the dimensionless variable $\tau = \alpha(t - t_0)$, $\eta = \sigma \alpha_m t_0$, $t_0 = x/u$, $\bar{C} = C/C_0$.

We search for the original of function $\tilde{C}$ by using the well-known rules of operator calculus (Goldstein 1953). Let $J(\eta, \tau)$ be the required function:

$$J(\eta, \tau) = L^{-1} \left[\frac{1}{s} \exp \left(-\frac{\eta s}{s+1} \right) \right]. \quad (6.30a)$$

We write an auxiliary transformation (Bateman and Erdelyi 1954)

$$L^{-1} \left[\frac{1}{s} \exp \left(\frac{\eta}{s} \right) \right] = I_0(2\sqrt{\eta\tau}). \quad (6.30b)$$

It is also known that when $f(\tau) = L^{-1}[g(s)]$, we have the following equation in Laplace transforms (Bateman and Erdelyi 1954)

$$e^{-b\tau} f(\tau) = L^{-1}[g(s+b)]. \quad (6.30c)$$

Therefore, multiplying function $I_0(\xi)$ in (6.30b) by $e^{-\tau}$ and both parts of this equation by $e^{-\eta}$, we can write

$$L^{-1} \left[\frac{1}{s+1} \exp \left(-\frac{\eta s}{s+1} \right) \right] = I_0(2\sqrt{\eta\tau}) e^{-(\eta+\tau)}. \quad (6.30d)$$

Whence, using the integral convolution rule, we obtain

$$\int_0^{\eta} e^{-(\lambda+\tau)} I_0(2\sqrt{\lambda\tau}) d\lambda = 1 - L^{-1} \left[\frac{1}{s} \exp \left(-\frac{\eta s}{s+1} \right) \right], \quad (6.30e)$$

thus,

$$\bar{C} \equiv J(\eta, \tau) = 1 - e^{-\tau} \int_0^{\eta} e^{-\lambda} I_0(2\sqrt{\lambda\tau}) d\lambda. \quad (6.31)$$

is the required solution. $I_0(z)$ is modified zero-order Bessel function of the first kind,

$$\eta = \sigma\alpha_m t_0, \quad \tau = \alpha_m(t - t_0), \quad t_0 = \frac{x}{u} < t. \quad (6.31a)$$

The function $J(\eta, \tau)$ is plotted in Fig. 6.3. Consider the main features of $J(\eta, \tau)$, often referred to as *Goldstein function* (Goldstein 1953; Ogata 1964, 1970; Eldor and Dagan 1972; Toride et al. 1993):

$$\begin{aligned} J(\eta, \tau) + J(\tau, \eta) &= 1 + \exp(-\eta - \tau) I_0(2\sqrt{\eta\tau}), \\ J(\eta, 0) &= e^{-\eta}, \quad J(\eta, \infty) = 1, \quad J(0, \tau) = 1, \quad J(\infty, \tau) = 0, \\ \frac{\partial J(\eta, \tau)}{\partial \eta} &= -\exp(-\eta - \tau) I_0(2\sqrt{\eta\tau}), \quad \frac{\partial J(\eta, \tau)}{\partial \tau} = \exp(-\eta - \tau) \sqrt{\frac{\eta}{\tau}} I_1(2\sqrt{\eta\tau}); \end{aligned}$$

here $I_1(y)$ is modified first-order Bessel function.

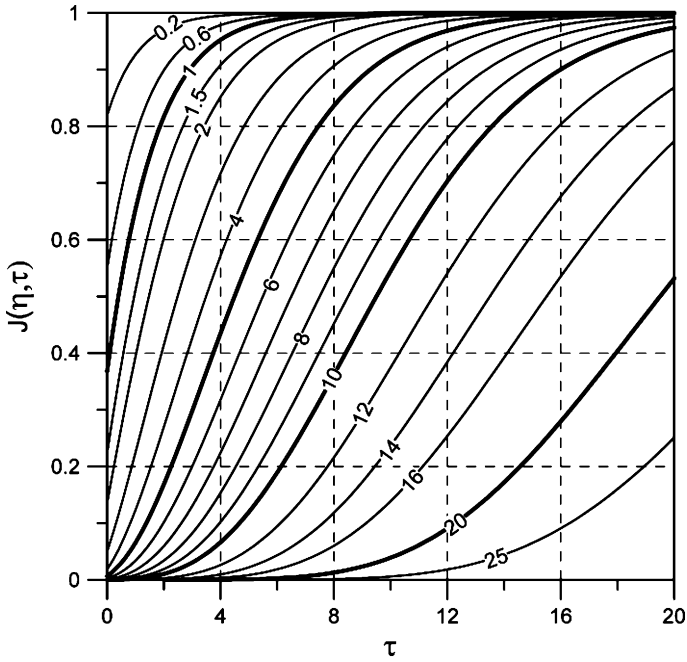
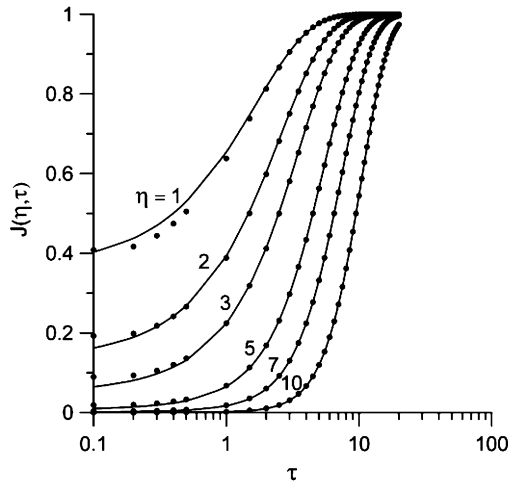


Fig. 6.3 Plots of function $J(\eta, \tau)$. Figures at curves are the values of parameter η

Fig. 6.4 Approximation of integral function (6.31) (*full lines*) by relationship (6.32) (*dots on the plot*)



When $\tau > 0.3$ and $\eta > 1.0$, function (6.31) can be adequately described by *Klinkenberg* asymptotic approximation (*Klinkenberg 1948*) (Fig. 6.4):

$$J(\eta, \tau) = \frac{1}{2} \operatorname{erfc} \left(\sqrt{\eta} - \sqrt{\tau} - \frac{1}{8\sqrt{\eta}} - \frac{1}{8\sqrt{\tau}} \right). \quad (6.32)$$

The mean solute concentration in blocks

$$\bar{C}_m = J'(\eta, \tau) = 1 - J(\tau, \eta). \quad (6.33)$$

It has been shown (Mathias et al. 2004) that as long as the mean solute residence time, $t_a = x(1 + \sigma)/u = x(\phi + \phi_m)/q$, is greater than the matrix block diffusion time, $t_m = 1/\alpha_m$ (6.16a), in other words $t_a > t_m$, the lumped capacitance model appears to be a plausible substitute for the exact solution of solute transport in fractured porous media. The ratio of t_a and t_m is a *Damkohler number*,

$$Da = \frac{t_a}{t_m} = \frac{x(1 + \sigma)\alpha_m}{u}. \quad (6.34)$$

In practice, the lumped capacitance model (6.31)/(6.33) is recommended to use for the moments satisfying the criterion

$$\tau > 0.3 - 0.5, \quad (6.35)$$

i.e., beyond the applicability limits of the unlimited matrix diffusion model (6.28). However, in this case, the assumption that the exchange regime between fractures and blocks is regular (quasi-steady) can also result in appreciable errors on the leading edge of the concentration wave ($\bar{C} < 0.5$), where the mass exchange is actually appreciably unsteady; therefore, it is desirable that an additional condition $qt \geq (\phi + \phi_m)x$ or $\tau \geq \eta$ is satisfied, ensuring the high saturation degree of the pore matrix by the solute (this condition commonly limits the calculation points by the domain of concentration variation $\bar{C} > 0.5$).

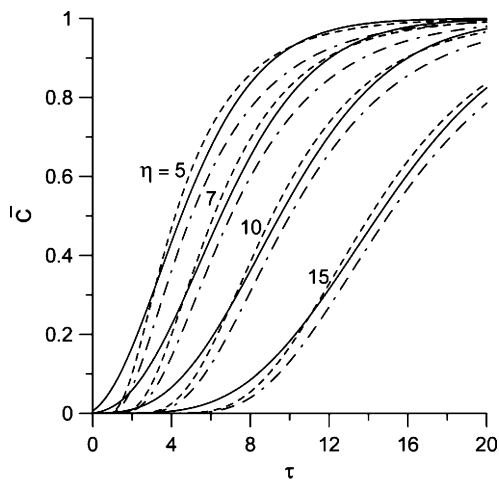
Multi-rate mass transfer formulations of transport typically refer to a system of deterministic equations that relate the one-dimensional multi-rate solute transport equation (6.19) and solute mass transfer between a mobile solution in fractures and porous blocks. The latter mechanism is characterized by memory function for multi-rate mass transfer (6.18) (Haggerty and Gorelick 1995; Benson and Meerschaert 2009). For multi-rate mass transfer model with discretely distributed mass transfer coefficient (6.18b), (6.18c), the solution of the problem in Laplace transforms (6.22) still has the same form with a correction introduced to account for variations in the capacity and mass exchange parameters:

$$\chi = p \left[1 + \sum_i^N \frac{\sigma_i \alpha_{mi}}{p + \alpha_{mi}} \right]. \quad (6.36)$$

6.1.3.4 Diffusion Asymptotics (Effective Single Porosity Model)

When $Da \gg 1$ ($t_a \gg t_m$) Eq. 6.19 reduces to the Fickian case. This means that at large η and τ (Fig. 6.5) the function (6.31) should have a diffusion asymptotics. Following this logic, we can write:

Fig. 6.5 Comparison of approximate solutions (6.37) (dashed lines) and (6.38) (dash-and-dot lines) with the exact solution (6.31) (full line) of the migration problem for fractured-porous rocks under lumped-capacitance assumption



$$\bar{C} \approx \frac{1}{2} \left[\operatorname{erfc} \left(\frac{\eta - \tau}{2\sqrt{\tau}} \right) + e^{\eta} \operatorname{erfc} \left(\frac{\eta + \tau}{2\sqrt{\tau}} \right) \right]. \quad (6.37)$$

By analogy with the well-known solution of advection–dispersion problem, the solution (6.31), where the basic function is defined by (6.37), can be written in an approximate form:

$$\bar{C} \approx 1 - \frac{1}{2} \operatorname{erfc} \left(\frac{\tau - \eta}{2\sqrt{\tau}} \right). \quad (6.38)$$

The acceptable agreement with the exact solution will be attained at $\tau > \eta > 5$ (Fig. 6.5). The solution (6.38) is written for the rear part of the concentration wave ($\bar{C} > 0.5$).

The asymptotic solutions (6.37) and (6.38) are close to the fundamental solution of the effective advection–dispersion equation (5.21) with apparent or asymptotic coefficients, defined by:

$$u^* = \frac{u}{1 + \sigma}, \quad D_L^* = \frac{\sigma}{\alpha_m(1 + \sigma)} (u^*)^2, \quad (6.39)$$

where D_L^* is the macrodispersion coefficient, $\sigma = \phi_m/\phi$. The first equation in (6.39) is the definition of the retarded velocity, and the second equation demonstrates the well-known fact that fracture–matrix exchange kinetics results in the solute front dispersion. The asymptotic behavior for large times controlled by macroscopic parameters (6.39) can be obtained by the moment analysis of an equivalent system of equations for first-order kinetic processes (Valocchi 1985; Dagan and Cvetkovic 1993; Govindaraju and Das 2007). For the median values of mass

exchange parameter, when the capacitance of rock blocks dominate in the system ($\phi \ll \phi_m$), we have

$$D_L^* = \alpha_m^{-1} (u^*)^2 = (S_b^2 D_m \phi_m^2)^{-1} q^2. \quad (6.39a)$$

For such conditions, the dependence (6.39a) directly follows from asymptotic solutions (6.37) and (6.38).

The stage of migration process considered above can be correlated with the *limiting asymptotic regime*, after whose onset, the solute concentrations in fractures and pore blocks become almost the same $C \approx C_m$. The relevant *effective porosity approach* and the described above dual porosity approach are usually examined as two alternative conceptual models of solute migration in fractured reservoirs (Arnold et al. 2000). In general, the dual porosity approach results in concentration breakthrough curves that differ significantly from the effective porosity approach and are characterized by earlier first arrival, greater apparent dispersion, and lower concentrations at later times. The effective-porosity approach, as implemented performance assessment analyses of saturated zone transport, is conservative compared to the dual porosity approach from the perspective of both solute concentrations and generally for travel times (Arnold et al. 2000).

6.1.3.5 Conclusive Remarks

Although the mathematical formalization of different levels of the mass-exchange in the schemes (models) considered above involves different physical assumptions, the critical characteristics are essentially the same, i.e., the specific surface area of the blocks (this characteristic indirectly accounts for block configuration and size), molecular (pore) diffusion coefficient, and the storage characteristics of fractures and blocks. Such parametric similarity of the model allows *analytical extrapolation* of parameters to be widely used in the description of processes with widely varying scales.

Overall, considering the statistical character of real fractured-porous media, the solutions given above will yield, of course, only benchmark estimates. However, when solving the problem in Laplace transforms, one also can, in principle, take into account variations in block size or porosity (within the limits of an elementary representative volume), resulting in that the diffusion-controlled saturation of blocks with the solute is nonuniform (Haggerty and Gorelick 1995; Gwo et al. 1998). Analysis shows that the blocks' having different sizes produces additional dispersion of solutes, whose extent is determined by the statistical parameters of the medium. In this case, the macrodispersion effects proper can be somewhat shadowed and distorted. The latter fact hampers the experimental assessment of the mean values of geometric characteristics of the porous medium determining the rate of mass-exchange processes in the scale of prediction estimates. Under real hydrogeological conditions, the effects caused by the superimposition of hydrodynamics macrodispersion also should be taken into account (see Sect. 6.3).

6.2 Generalized Solutions

Here we will leave the simplest one-dimensional formulation of solute transfer problem in fractured-porous media and abandon the assumption that the replacement of solution along fractures is ideal.

6.2.1 A Streamline-Based Approach

The above relationships, obtained for one-dimensional flow in porous medium can be used to analyze the migration in two- and three-dimensional flows. For this purpose, the problems of multidimensional flow are converted into one-dimensional formulation by considering the process as taking place along streamlines. Such conversion can be made in several ways (both analytical and based on numerical modeling), allowing one to describe flow structure (identify streamlines) and determine the field of Darcy velocities.

In such case, the basic solutions for main asymptotic models (6.24) and (6.31) may change only in terms of the structure of the dimensionless groups (6.24a) and (6.31a) that determine them:

- for unlimited matrix diffusion model

$$\eta = \sigma \lambda_m t_0, \quad \tau = \lambda_m (t - t_0); \quad (6.40a)$$

- for lumped capacitance model

$$\eta = \sigma \alpha_m t_0, \quad \tau = \alpha_m (t - t_0). \quad (6.40b)$$

In the relationships given here, t_0 essentially is the time parameter of the characteristic solution of advection transport equation in a homogeneous medium. For example, for two-dimensional horizontal flow, considered in the coordinates of flow velocity potential $\varphi(x, y)$ and flow function $\psi(x, y)$, it follows from (1.75) that

$$t_0 = \phi \int_{\varphi_0}^{\varphi} \frac{d\varphi'}{q^2(\varphi', \psi)}, \quad (6.41)$$

where $q^2(\varphi, \psi) = \left(\frac{\partial \varphi}{\partial x}\right)^2 + \left(\frac{\partial \varphi}{\partial y}\right)^2 = q_x^2 + q_y^2$, φ_0 is the value of potential function corresponding to the initial position of the concentration front on the streamline ψ . As before, in the basic solutions, $0 < \bar{C} \leq 1$ when $t > t_0$ and $\bar{C} = 0$ when $t \leq t_0$.

A rigorous proof of the feasibility to reduce three-dimensional migration problems (with no allowance made for dispersion) to quasi-one-dimensional problems can be obtained, for example, through representing the two-dimensional operator

$\mathbf{u} \cdot \nabla C$ in Eq. 1.12 in the form 1.73 with the subsequent consideration of an equivalent system of ordinary differential equations (see also Sect. 1.2.2).

6.2.2 Application of the Convolution Property of the Laplace Transform for Solving the Problem of Solute Advective Dispersion in Dual Porosity Systems

Essentially, the method consists in the search for a form of solution of mass transport equation in a dual porosity medium, such that two components of migration process can be identified, separately reflecting the effects of advection dispersion and kinetic mass exchange. This becomes possible when there exists a linear dependence between Laplace transforms of concentration C in the permeable zones of the bed and reduced mass transfer rate:

$$\tilde{W}_{sr} = \tilde{g}(p) \left(\tilde{C} - \frac{C^0}{p} \right); \quad (6.42)$$

here $\tilde{g}(p)$ is the Laplace transform of the memory function (Sect. 6.1.2), whose form, (6.21a) and (6.21b), depends on the accepted regime of mass exchange within the dual porosity medium; C^0 is background (initial) concentration.

In this case, the Laplace transforms of the initial differential equations, accounting for micro- and macro-dispersion models, are formally of the same type and differ only in the coefficients at the transform of the time derivative of concentration ($\partial C / \partial t$).

Indeed, from the general equation (6.1), it follows that with $W_{sr} = 0$ (a homogeneous aquifer), we have

$$\left(\tilde{C}' - \frac{C^0}{p} \right) p + A(\tilde{C}') = 0, \quad (6.43a)$$

while with $W_{sr} < 0$ (dual porosity system, Eq. (6.2)),

$$\left(\tilde{C} - \frac{C^0}{p} \right) (p + \sigma \tilde{g}(p)) + A(\tilde{C}) = 0, \quad (6.43b)$$

where $A(\tilde{y}) = \nabla \cdot (\mathbf{u} \tilde{y} - \mathbf{D} \nabla \tilde{y})$ is a linear advection–dispersion differential operator (with respect to the space coordinate x), $\tilde{C}'$ and $\tilde{C}$ are the Laplace transforms of the current concentrations C' and C in models of groundwater reservoirs with single or dual porosity structures.

The transforms considered below have been proposed for describing nonequilibrium linear processes (De Smedt and Wierenga 1979; Toride et al. 1993; De Smedt et al. 2005; Veling 2005; De Smedt 2006). In this section, they are developed as

applied to the migration conditions in a fractured-porous reservoir with the use of asymptotic (utmost) models.

First we consider the basic solution (6.22a) of the equation for the case of an *impulse* input, approximated by Dirac delta function. When $\lambda_m = 0$ or $\alpha_m = 0$, this solution reduces to the solution in Laplace transforms of the classic advection–dispersion equation for the same input signal. Thus, we can write the identity

$$\tilde{C}_i(p) = \tilde{C}'_i(p + \sigma \tilde{g}(p)); \quad (6.44)$$

hereafter, to simplify the formulas, we assume $C^0 = 0$.

In the case of a *step-wise* input concentration, the solutions of the problem in Laplace transforms are identical only with the transform parameter p replaced by the sum $p + \sigma \tilde{g}(p)$ in the transform of the time derivative $C'(t)$ of concentration. An equivalent mathematical expression has the form

$$\frac{\partial}{\partial t} C(p) = \frac{\partial}{\partial t} C'(p + \sigma \tilde{g}(p)). \quad (6.45)$$

The Eq. 6.45 reflects the fact that solutions for Dirac delta function can be obtained by differentiating the solutions for step-wise functions (C' and C) with respect to time. From (6.45) we have

$$\tilde{C}(p) = \frac{1}{p} \frac{\partial}{\partial t} C'(p + \sigma \tilde{g}(p)). \quad (6.45a)$$

Further reasoning is based on successive (“two-step”) Laplace transform for (6.44) and (6.45), which can be represented in the operator form as (De Smedt and Wierenga 1979; Toride et al. 1993)

$$L\{L[f(t_1, t_2), t_2 \rightarrow p], t_1 \rightarrow p\} = L\left\{\int_0^t f(\tau, t - \tau) d\tau, t \rightarrow p\right\}. \quad (6.46)$$

This means that the successive Laplace transform of function f is equal to the ordinary, one-sided Laplace transform of generalized integral convolution of this function (L denotes direct Laplace transform (1.107)).

Let us write the equality for *impulse* in Laplace transforms (6.22a) as

$$\tilde{C}_i(x, p_1, p_2) = \frac{p_1}{p_2} \tilde{C}'_i(p_1 + \sigma \tilde{g}(p_2)), \quad (6.47)$$

where $p_1 = p_2 = p$, and different subscripts are used to emphasize the two-step character of the inverse passage to the original of the function. The first step of such passage with respect to p_1 yields

$$L[C_i(x, t_1, t_2), t_2 \rightarrow p_2] = \frac{\partial}{\partial t_1} \left[\frac{1}{p_2} \exp(-\sigma \tilde{g}(p_2) t_1) C'_i(x, t_1) \right], \quad (6.48a)$$

The second step with respect to p_2 yields the following formula:

$$C_i(x, t_1, t_2) = \frac{\partial}{\partial t_1} \left\{ L^{-1} \left[\frac{1}{p_2} \exp(-\sigma \tilde{g}(p_2) t_1) \right]_{p_2 \rightarrow t_2} C'_i(x, t_1) \right\}. \quad (6.48b)$$

In view of (6.46)

$$C_i(x, t) = \int_0^t \frac{\partial}{\partial t_1} \left\{ L^{-1} \left[\frac{1}{p_2} \exp(-\sigma \tilde{g}(p_2) t_1) \right]_{p_2 \rightarrow t_2} C'_i(x, t_1) \right\} dt_1, \quad (6.48c)$$

or

$$C_i(x, t) = \int_0^t \frac{\partial}{\partial \theta} \left\{ L^{-1} \left[\frac{1}{p_2} \exp(-\sigma \tilde{g}(p_2) \theta) \right]_{p_2 \rightarrow t-\theta} C'_i(x, \theta) \right\} d\theta. \quad (6.48d)$$

The originals of functions, $L^{-1}(\tilde{y})$, entering the expression under integral sign in (6.48c)–(6.48d), are known (see 6.1.3.). Therefore, the solution of the problem for the two models can be represented in the following dimensionless form:

– unlimited matrix diffusion model

$$\bar{C}_i(\eta, \tau) = \int_0^\tau \frac{\partial}{\partial \tau'} \left[\operatorname{erfc} \frac{\sigma \tau'}{2\sqrt{\tau - \tau'}} \bar{C}'_i(\eta, \tau') \right] d\tau', \quad \tau = \lambda_m t; \quad (6.49)$$

– lumped capacitance model

$$\bar{C}_i(\eta, \tau) = \int_0^\tau \frac{\partial}{\partial \tau'} [J(\sigma \tau', (\tau - \tau')) \bar{C}'_i(\eta, \tau')] d\tau', \quad \tau = \alpha_m t. \quad (6.49a)$$

The form of solutions (6.49) and (6.49a) implies the normalization of function C_i and coefficients of hydrodynamic-dispersion model. For example, the solution for momentum becomes

$$\bar{C}'_i(\eta, \tau) = \frac{1}{2\sqrt{\pi \bar{D} \tau}} \exp \left[-\frac{(\eta - \tau)^2}{4\bar{D} \tau} \right]; \quad (6.49b)$$

the dimensionless groups are:

$$\bar{C}_i = \frac{\phi S u}{\alpha_m M} C_i, \quad \eta = \frac{\alpha_m x}{u}, \quad \bar{D} = \frac{\alpha_m D_L}{u^2} \quad (6.49c)$$

(S is flow cross section area).

Analysis of solution (6.49a), written for the lumped capacitance model (Huang et al. 2006), shows it to be identical to the following solution of the problem under consideration (Goltz and Roberts 1986; Black and Kipp 1983; Davis et al. 2000; Veling 2005):

$$\bar{C}_i(\eta, \tau) = \bar{C}'_i(\eta, \tau) \exp(-\sigma\tau) + \sigma \int_0^\tau H(\tau, \tau') \bar{C}'_i(\eta, \tau') d\tau', \quad (6.50)$$

$$H(\tau, \tau') = \frac{\sqrt{\tau'}}{\sqrt{\sigma(\tau - \tau')}} \exp[-(\tau - \tau') - \sigma\tau'] I_1(2\sqrt{(\tau - \tau')\sigma\tau'}), \quad (6.50a)$$

$I_1(\cdot)$ is modified first-order Bessel function.

By analogy with the performed transforms, in the case of the *step-wise* function (6.45a), we have

$$L[C(x, t_1, t_2), t_2 \rightarrow p_2] = \frac{1}{p_2} \exp(-\sigma \tilde{g}(p_2)t_1) \frac{\partial C'(x, t_1)}{\partial t}, \quad (6.51)$$

$$C(x, t_1, t_2) = L^{-1} \left[\frac{1}{p_2} \exp(-\sigma \tilde{g}(p_2)t_1) \right]_{p_2 \rightarrow t_2} \frac{\partial C'(x, t_1)}{\partial t}. \quad (6.51a)$$

In view of (6.46)

$$C(x, t) = \int_0^t L^{-1} \left[\frac{1}{p_2} \exp(-\sigma \tilde{g}(p_2)t_1) \right]_{p_2 \rightarrow t_2} \frac{\partial C'(x, t_1)}{\partial t_1} dt_1, \quad (6.51b)$$

or

$$C(x, t) = \int_0^t L^{-1} \left[\frac{1}{p_2} \exp(-\sigma \tilde{g}(p_2)\theta) \right]_{p_2 \rightarrow t-\theta} \frac{\partial C'(x, \theta)}{\partial \theta} d\theta. \quad (6.51c)$$

In the explicit form we obtain:

– unlimited matrix diffusion model

$$\bar{C}(\eta, \tau) = \int_0^\tau \frac{\partial \bar{C}'(\eta, \tau')}{\partial \tau'} \operatorname{erfc} \frac{\sigma \tau'}{2\sqrt{\tau - \tau'}} d\tau', \quad \tau = \lambda_m t; \quad (6.52)$$

– lumped capacitance model

$$\bar{C}(\eta, \tau) = \int_0^\tau \frac{\partial \bar{C}'(\eta, \tau')}{\partial \tau'} J(\sigma \tau', (\tau - \tau')) d\tau', \quad \tau = \alpha_m t, \quad \sigma = \frac{\phi_m}{\phi}; \quad (6.52a)$$

for the mean concentration in the pore matrix:

$$\bar{C}_m(\eta, \tau) = \int_0^\tau \frac{\partial \bar{C}'(\eta, \tau')}{\partial \tau'} [1 - J((\tau - \tau'), \sigma \tau')] d\tau'. \quad (6.52b)$$

For example, under the conditions of the fundamental problem (constant initial and boundary conditions), the differentiation of (1.104) yields

$$\frac{\partial \bar{C}'}{\partial \tau} = \frac{1}{4\sqrt{\pi \bar{D} \tau}} \left\{ \frac{\eta + \tau}{\tau} \exp \left[-\frac{(\eta - \tau)^2}{4\bar{D} \tau} \right] + \exp \left(\frac{\eta}{\bar{D}} \right) \frac{\eta - \tau}{\tau} \exp \left[-\frac{(\eta + \tau)^2}{4\bar{D} \tau} \right] \right\}. \quad (6.52c)$$

The structure of formula (6.52a) for the conceptual model with lumped capacitance coincides with the solutions of problems of nonequilibrium sorption in a flow in porous medium (Lindstrom and Stone 1974, p. 581; van Genuchten and Wagenet 1989, p. 1306).

Formulas (6.52) and (6.52a) have a simple physical interpretation: the integrals that determine them take into account the joint effect of two factors: advection and dispersion, on the one hand, and mass exchange processes, on the other hand; the latter factor being assigned a weight coefficient determined by the effect of the first factor, depending on time interval $t - \theta$. Thus, the final result is based on two partial solutions that are already known.

The results of numerical calculations by formula (6.52), in which the derivative in the integrand was defined by (6.52c), are given in Fig. 6.6. The same plot shows curves corresponding to the limiting solutions $\lambda_m = 0$ (a homogeneous aquifer) and piston-like displacement $\delta_L = 0$ (Lauverier solution). The hydrodynamic dispersion in fractures can be seen to cause additional dispersion of solute in the aquifer, accelerating its transport in low concentrations and hampering the propagation of high concentrations. The result is that the solution (6.24) for ideal replacement in fractures appreciably underestimates the concentrations at the leading edge of the solute wave. However, the role of microdispersion noticeably declines with increasing domain size; its effect on the terminal parts of indicator plots, corresponding to long-term interaction between fractures and blocks, is also insignificant. Overall, the hydrodynamic dispersion in fractures can be of importance only at the level of local tracer experiments (see 8.1.4.2).

The solving of the problem of the three-dimensional dispersion from an impulse source in an dual porosity medium also yields the formula (6.50) (Carnahan and Remer 1984; Goltz and Roberts 1986), where:

$$\bar{C}'_i(\eta, \xi, \sigma, \tau) = \frac{1}{8(\pi \tau)^{3/2} (\bar{D}_x \bar{D}_y \bar{D}_z)^{1/2}} \exp \left[-\frac{(\eta - \tau)^2}{4\bar{D}_x \tau} - \frac{\xi^2}{4\bar{D}_y \tau} - \frac{\omega^2}{4\bar{D}_z \tau} \right], \quad (6.53)$$

$$\bar{C}_i = \frac{\phi u^3}{\alpha_m^3 M} C_i, \quad \eta = \frac{\alpha_m x}{u}, \quad \xi = \frac{\alpha_m y}{u}, \quad \omega = \frac{\alpha_m z}{u}, \quad \tau = \alpha_m t, \quad \bar{D}_l = \frac{\alpha_m D_l}{u^2}.$$

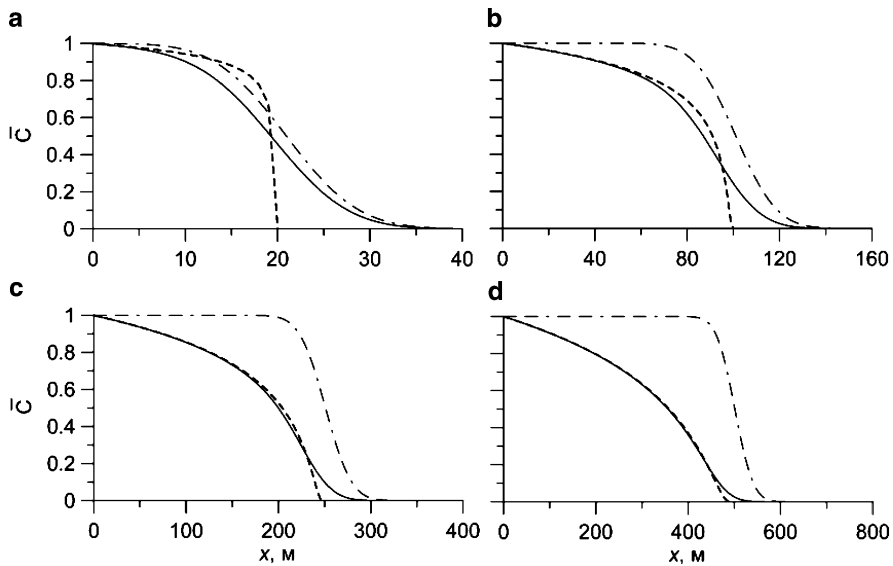


Fig. 6.6 Results of comparison of limiting (*dashed* lines) Lauerier solutions (6.24) and (*dash-and-dot*) microdispersion solutions (1.104) with (*full* lines) the exact solution (6.52) for the problem of one-dimensional flow in a fractured-porous aquifer. (a) $t = 2$, (b) 10, (c) 25, (d) 50 d. The initial data: $u = 10 \text{ md}^{-1}$, $D_L = 10 \text{ md}^{-1}$ ($\delta_L = 1 \text{ m}$); $\sigma^2 \lambda_m = 1 \times 10^{-2} \text{ d}^{-1}$

The form of function $H(\tau, \tau')$ remains unchanged (6.50a), the fact that can be attributed to the similarity of solutions in Laplace transforms for the problems of one-dimensional and three-dimensional dispersion with a change of the complex variable according to (6.44).

6.3 Solute Transport in Heterogeneous Dual Porosity Media (Qualitative Analysis)

Solute transport description under field conditions is complicated by the hydraulic conductivity heterogeneity of the fracture network. Therefore, despite numerous studies of the mobile-immobile mass transfer approach, very few studies have been conducted to establish the applicability and usefulness of the discussed above dual domain approach and models for characterizing field-scale solute transport in heterogeneous media (Feehley et al. 2000; Xu and Hu 2004). Of great use in the context of the problem considered here are the results of Dagan and Cvetkovic (1993), focused on the study of first-order kinetics (adsorption) in a heterogeneous aquifer. Because the two models, adsorption kinetics and diffusion exchange kinetics (first-order mass transfer coefficient approach), are physically similar and mathematically

equivalent, the major conclusions from [Dagan and Cvetkovic \(1993\)](#) can be extended to solute transport in fractured-porous media.

The obtained analytical expressions ([Dagan and Cvetkovic 1993](#)) and their comparison with the appropriate relationships for mass transfer in single-porosity media suggests that the macrodispersion in heterogeneous dual-porosity media is complex: attempts to describe mass transfer under classical Fickian advection–dispersion model require one, in the general case, to introduce coefficients, which are complex functions of the spatial and temporal scale of the process. Classical diffusion asymptotics appear only in long migration stages, where solute dispersion is governed by the joint contribution variations of Darcy velocity field and the kinetics of solute exchange between fractures and porous matrix.

The behavior of the system becomes significantly unsteady, when the characteristic time of its “matrix” relaxation (corresponding to the period when the saturation of porous blocks with solute was sufficiently high) $t_m = 1/\alpha_m$ is appreciably higher than the time required for the advection front to cover the distance equivalent to the unit correlation scale $t_h = l_x(1 + \sigma)/u$: $t_m/t_h = u/[l_x\alpha_m(1 + \sigma)] \gg 1$, the features mentioned above manifest themselves even when asymptotic diffusion regime is attained in an equivalent homogeneous bed, i.e., $t/t_h \gg 1$ (here l_x is a characteristic linear scale of permeability correlation function in the direction x , $\sigma = \phi_m/\phi$).

However, for less stringent conditions, corresponding to the opposite case $t_m/t_h \ll 1$, with the simultaneous fulfillment of the criterion $t/t_h \gg 1$, the system behaves similarly to a bed with homogeneous capacitance with the total porosity $\phi^* = \phi + \phi_m$, such that the effects of macrodispersion can be described in the context of conventional concepts of stochastic theory by incorporating some additional linear terms, related to coefficients α_m and σ , into the formulas for calculations. Thus, it can be shown ([Dagan and Cvetkovic 1993](#)) that variations in the coefficient of longitudinal macrodispersion, $D_L^*(t)$, can be described by the expression

$$D_L^*(t) = \frac{\sigma}{\alpha_m(1 + \sigma)} u^{*2} + \frac{\sigma_Y^2 l_x}{\tau} (\tau + e^{-\tau} - 1) u^*, \quad (6.54)$$

where σ_Y^2 is the root-mean-square deviation at lognormal permeability distribution of the medium; $\tau = but/l_x$; $b = 1$ at $l_x \gg l_z$ (a stratified system); $b = 8/15 \approx 1/2$ at $l_x = l_z$ (an isotropic medium). The range $b = 1 - 1/2$ embraces the anisotropic systems with $\kappa_l = l_z/l_x < 1$, l_z is the linear scale of permeability correlation function in the z -direction.

In the limiting case, when we simultaneously have $t/t_m \gg 1$ and $t/t_h \gg 1$, which corresponds to the case when the history of the migration process is much longer than the characteristic times of system relaxation, the effective coefficient of longitudinal macrodispersion D_L^* stabilizes, reaching the limiting value:

$$D_L^* = \frac{\sigma}{\alpha_m(1 + \sigma)} u^{*2} + \sigma_Y^2 l_x u^*. \quad (6.54a)$$

Thus, we have come to a simple system of two constants, the first being responsible for dispersion due to the kinetics of solute exchange between fractures and blocks, and the second, for dispersion due to flow velocity variations in the aquifer with heterogeneous permeability. This allows the contribution of each component in the asymptotic regime to be readily assessed.

Further analysis of the obtained statistical moments, reflecting the parameters responsible for transverse dispersion (Dagan and Cvetkovic 1993), has shown that the more intense mass exchange between fractures and blocks, the less the extent of transverse dispersion. As was the case with homogeneous-capacitance rocks, the estimated coefficients of transverse dispersion at very large time ($t \gg t_h$) tend to decrease, so that the appropriate asymptotic values $\delta_{T_H}^*$ and $\delta_{T_V}^*$ can be expected to be close to the local characteristics, $D_m + \delta_{T_{H(V)}}$.

The results of this analysis suggest that in many real cases involving long-term contamination of rocks with pronounced dual porosity ($\phi_m \gg \phi$) and sufficiently disintegrated by fracture systems, the effect of variations in permeability on the macrodispersion properties of the environment is secondary. These conclusions were confirmed by Eulerian analytical method developed for nonreactive solute transport in heterogeneous, dual permeability media where the hydraulic conductivities in fracture and matrix domains are both assumed to be stochastic processes (Xu and Hu 2004). It was clearly shown that for plume spreading in the longitudinal direction, the interregional mass diffusion is much more important than the dispersion caused by heterogeneity in each domain.

6.4 Adsorption and Decay

Along with matrix diffusion, adsorption and contaminant destruction (decay) are among the key processes impacting the efficiency of natural attenuation in the subsurface presented by fractured rocks. These processes indirectly influence also the dispersion of the dissolved species in the fracture network.

6.4.1 Adsorption

The calculation formulas take into account two types of adsorption – on the surface of porous blocks and in their pore space. When *linear* sorption is considered, the appropriate parameters of block fracturing (ϕ) and porosity (ϕ_m) increase by $\Delta\phi = K_a S_b$, $\Delta\phi_m = K_d \rho_b$, such that the retardation factors associated with fracture system and matrix are determined by equations as follows

$$R = 1 + \Delta\phi/\phi, R_m = 1 + \Delta\phi_m/\phi_m; \quad (6.55)$$

here K_d is the surface sorption coefficient of the fracture system, K_d is the linear distribution coefficient for porous matrix, ρ_b is rock density. The contribution of adsorption processes in the two continuums varies over space and time: the sorption on fracture walls is of greatest importance at the earlier stages of migration and in the frontal zone of the propagating solution. The role of sorption in porous matrix increases with the development of diffusion at the later stages of migration.

Reactive component transport analysis based on sorption equilibrium approach can be carried out with the help of all models considered above (Sects. 6.1–6.3) with corrections using the following transformations

$$t_0 \rightarrow t_0^s = \frac{xR}{u}, \quad \lambda_m, \alpha_m \rightarrow \lambda_m^s = \frac{\lambda_m}{R_m}, \quad \alpha_m^s = \frac{\alpha_m}{R_m}, \quad \sigma \rightarrow \sigma^s = \frac{R_m \phi_m}{R\phi}, \quad (6.56)$$

where the superscript s refers to the system of the component being sorbed. From here it can be seen that the characteristic migration time of absorbable particles along fractures, t_0^s , and the ratio of total contaminant mass in the porous matrix to its mass in the fractures at sorption equilibrium, σ^s , increases, and the values of mass exchange parameters (λ_m^s or α_m^s , used to describe fracture-matrix exchange kinetics) decrease relative to the physical models with no sorption. Under asymptotic mass transport regime, fractured porous medium behaves as a single-porosity one with a total capacity of $R\phi + R_m\phi_m$ instead of $R\phi$, thus matrix retardation factor is defined as (Maloszewski and Zuber 1985; Carrera et al. 1998):

$$R_{fm} = 1 + \frac{R_m\phi_m}{R\phi}. \quad (6.57)$$

Nonlinear adsorption (convex isotherms) in fractured-porous rocks, similarly to migration in homogenous media, facilitates the suppression of solute dispersion, as can be seen from the analysis of some limiting calculation schemes (Mironenko and Rumynin 1986) and derived from numerical modeling results (Kumar 2008).

6.4.2 Decay

In a dual porosity system, the decay of unstable components (Sect. 1.5.2) takes place not only in fractures but also within the volume of solution, which saturates the pore matrix through diffusion.

6.4.2.1 Single-Stage Decay

The solute mass balance equation in the case of diffusion in fractures can be written as

$$\frac{\partial C}{\partial t} + \lambda C + u \frac{\partial C}{\partial x} - D_L \frac{\partial^2 C}{\partial x^2} + \sigma W_{sr} = 0. \quad (6.58)$$

As before (see Sect. 6.1.2), we will consider situations for two major laws of mass exchange between the solution moving in fractures and the immobile pore water:

- for unlimited matrix diffusion model

$$W_{sr} = -\lambda_m^{1/2} \left[\lambda^{1/2} (\operatorname{erfc} \sqrt{\lambda t} - 1) - \frac{\exp(-\lambda t)}{\sqrt{\pi t}} \right] C; \quad (6.59a)$$

- for lumped capacitance model

$$\begin{cases} W_{sr} = \frac{\partial C_m}{\partial t} + \lambda C_m, \\ \frac{\partial C_m}{\partial t} = \alpha_m (C - C_m) - \lambda C_m. \end{cases} \quad (6.59b)$$

Taking the Laplace transform of both sides of these equations, we obtain the ordinary differential equation (6.21), in which, as before, the function $\chi(p)$ has two major representations:

$$\chi = p + \lambda + \sigma \sqrt{\lambda_m(p + \lambda)}, \quad (6.60a)$$

$$\chi = p + \lambda + \frac{\sigma \alpha_m (p + \lambda)}{(p + \alpha_m + \lambda)}. \quad (6.60b)$$

The Eq. 6.21 with constant boundary and initial conditions $C(t, 0) = C_0$ $C(0, x) = 0$, respectively, has the solution (6.22). In the case of piston-like motion of the solute in the aquifer, the solution (6.22) can be transformed to the form of (6.23).

The reverse passage to the original of function $\tilde{C}$ (6.23) for the scheme with unlimited capacitance was made in the paper Tang et al. (1981):

$$\bar{C} = \frac{1}{2} e^{-\lambda t_0} \left[e^{-\eta} \operatorname{erfc} \left(\frac{\eta}{2\sqrt{\tau}} - \sqrt{\tau} \right) + e^{\eta} \operatorname{erfc} \left(\frac{\eta}{2\sqrt{\tau}} + \sqrt{\tau} \right) \right] \quad (6.61)$$

($\bar{C} = C/C_0$, $\eta = \sigma t_0 \sqrt{\lambda \lambda_m}$, $\tau = \lambda(t - t_0)$) The same paper gives a more general solution ($D_L > 0$). With $t \rightarrow \infty$, formula (6.61) yields the steady-state concentration distribution

$$\bar{C} = \exp[-\lambda t_0 (1 + \beta)], \quad (6.62)$$

where

$$\beta = \sigma \sqrt{\lambda_m / \lambda}. \quad (6.62a)$$

Thus, as was the case with homogeneous rocks (Sect. 1.5.2), the decay process results in the formation of quasi-steady pollution plumes. However, because of the solute exchange between fractures and blocks, the plumes are more localized: the length of the transition zone Δx_λ is less $(1 + \sigma \sqrt{\lambda_m / \lambda})$ times than that in a single porosity aquifer.

To find the respective solutions for the calculation scheme with lumped capacitance, we write (6.23) as

$$\tilde{C} = e^{-\eta} \left\{ \frac{C_0}{p} e^{-t_0(p+\lambda)} \right\} + e^{-\eta} \left\{ \frac{C_0}{p} e^{-t_0(p+\lambda)} \right\} \times \left\{ \exp \left[\frac{\alpha_m \eta}{p + \alpha_m + \lambda} \right] - 1 \right\} \quad (6.63)$$

($\eta = \sigma \alpha_m t_0$). In such case, a tabulated original is available for any factor in curly brackets. Now, using the theorem of integral convolution for the second summand in (6.63), we finally obtain

$$\bar{C} = e^{-\lambda t_0} e^{-\eta} \left\{ 1 + \int_0^{\tau} e^{-z(1+\gamma)} \sqrt{\frac{\eta}{z}} I_1(2\sqrt{\eta z}) dz \right\}, \quad (6.64)$$

where $\eta = \sigma \alpha_m t_0$, $\tau = \alpha_m(t - t_0)$, $\gamma = \lambda/\alpha_m$, $I_1(y)$ is modified Bessel function.

Additional transformations allow (6.64) to be reduced to the form more convenient for practical analysis:

$$\bar{C} = e^{-\lambda t_0 - \eta'} J(\eta', \tau'), \quad (6.64a)$$

$$\tau' = \tau(1 + \gamma) = (\alpha_m + \lambda)(t - t_0), \quad \eta' = \frac{\eta}{1 + \gamma} = \frac{\sigma \alpha_m^2 t_0}{(\alpha_m + \lambda)}, \quad (6.64b)$$

$J(\eta', \tau') = 1 - e^{-\tau'} \int_0^{\eta'} e^{-z} I_0(2\sqrt{\tau' z}) dz$ is Goldstein function, plotted in Fig. 6.3.

Thus, the decay of solute in a fractured-porous bed, where mass exchange between fractures and blocks is quasi-steady, can be described by the available basic solutions for a non-reactive component with transformed coordinate axes, where the dimensionless variables η and τ are replaced by η' and τ' according to (6.64b), and the concentration function is multiplied by $\exp[-\lambda t_0(1 + \sigma \alpha_m/(\alpha_m + \lambda))]$. The system of equations, describing the migration of a nonconservative component subject to kinetic-controlled sorption by rock (Eldor and Dagan 1972) can be also reduced to this problem.

The steady-state solution (with $t \rightarrow \infty$), since $J(\eta, \infty) = 1$, has the form (6.62) with

$$\beta = \frac{\sigma \alpha_m}{(\alpha_m + \lambda)}. \quad (6.65)$$

The exact solution of the problem considered here has been obtained for the conditions of migration in a fractured massif with regularly spaced fractures separating porous blocks with slab shape (Sudicky and Frind 1982; Ling and Liu 2002). The stationary asymptotics of this solution in our notations has the form (6.62) with

$$\beta = \sigma \sqrt{\frac{\lambda_m}{\lambda}} \operatorname{th} \sqrt{\frac{\lambda}{\lambda_m}}. \quad (6.65a)$$

We assumed here that, with the distance m_b between the neighboring fractures, the specific surface of the blocks will be $2/m_b$, such that $\lambda_m = S_b^2 D_m$. When the argument of the hyperbolic tangent is large ($\operatorname{th}(z)|_{z \rightarrow \infty} = 1$), the formula (6.65a) exactly coincides with (6.62a) (infinite capacitance scheme). Conversely, when the argument of hyperbolic tangent is small ($\operatorname{th}(z)|_{z \rightarrow 0} = z$), we have $\beta = \sigma = \phi_m/\phi$, which corresponds to (6.65a) at $\lambda_m \gg \lambda$. In this case, clearly, the dispersion of the stationary front is governed by the decay constant λ and the velocity $u^* = q/(\phi + \phi_m)$, i.e., it does not depend on mass-exchange characteristics of the blocks. Now the general solution of the steady-state problem of transport in a fracture adjacent to a finite-size block becomes (Ling and Liu 2002)

$$\bar{C} = \exp\left(-\frac{\lambda x}{u^*}\right), u^* = \frac{u}{(1 + \sigma)}, \quad (6.65b)$$

similar to the solution of the transport problem of a decaying solute (with a retardation factor $R = 1 + \sigma$) in an equivalent homogeneous aquifer.

6.4.2.2 Two-Member Decay Chain

If migration of parent and daughter nonreactive isotopes is considered, a generalized system of one-dimensional governing equations can be written as

$$\frac{\partial C_1}{\partial t} + u \frac{\partial C_1}{\partial x} - D_L \frac{\partial^2 C_1}{\partial x^2} + \sigma W_{sr1} = -\lambda_1 C_1, \quad (6.66a)$$

$$\frac{\partial C_2}{\partial t} + u \frac{\partial C_2}{\partial x} - D_L \frac{\partial^2 C_2}{\partial x^2} + \sigma W_{sr2} = -\lambda_2 C_2 + \lambda_1 C_1, \quad (6.66b)$$

$$\frac{\partial C_{m1}}{\partial t} - \frac{D_m}{\rho^{v-1}} \frac{\partial}{\partial \rho} \left(\rho^{v-1} \frac{\partial C_{m1}}{\partial \rho} \right) = -\lambda_1 C_{m1}, \quad (6.66c)$$

$$\frac{\partial C_{m2}}{\partial t} - \frac{D_m}{\rho^{v-1}} \frac{\partial}{\partial \rho} \left(\rho^{v-1} \frac{\partial C_{m2}}{\partial \rho} \right) = -\lambda_2 C_{m2} + \lambda_1 C_{m1}, \quad (6.66d)$$

$$W_{sri} = -S_b D_{mi} \left\langle \frac{\partial C_{mi}}{\partial \rho} \right\rangle_{\rho \in S}, \langle C_{mi} = C_i \rangle_{\rho \in S}, \left. \frac{\partial C_{mi}}{\partial \rho} \right|_{\rho = \rho_m} = 0. \quad (6.66e)$$

The first two equations of the system describe the advection–dispersion transport of (subscript 1) the parent and (subscript 2) daughter components in fractures; the other two equations are a formalization of the diffusion process in pore blocks with isometric shape (see Sect. 6.1.2); the last Eqs. (6.66e) reflect the coupling conditions of processes in fractures and blocks (zero mass flow is specified in the center of each

block and it is assumed that $\rho = \rho_m$); here, the subscript m characterizes pore matrix. Hereafter, we restrict ourselves to the analysis of a simplified model corresponding to the scheme of unlimited matrix diffusion with $D_L = 0$, meaning it to be applied to the interpretation of monitoring data of global isotopic tracers in aquifers associated with fractured rock massifs.

The appropriate solutions (commonly, for transport in a single fracture), obtained by different methods for an impulse input signal, can be found in [Sudicky and Frind \(1984\)](#), [Cormenzana \(2000\)](#), as well as [Sun and Buscheck \(2003\)](#). The solution of the problem ([Cormenzana 2000](#)), found with the use of Laplace transform, in our notations (see Sect. 6.1) is conveniently written as

$$\bar{C}_1^i = \frac{C_1^i \phi S x}{M_1} = \exp(-\bar{\lambda}_1 \bar{t}) \frac{\sqrt{\bar{\lambda}}}{\sqrt{4\pi(\bar{t}-1)^3}} \exp\left[-\frac{\bar{\lambda}}{4(\bar{t}-1)}\right], \quad (6.67a)$$

$$\begin{aligned} \bar{C}_2^i &= \frac{C_2^i \phi S x}{M_1} \\ &= \frac{\bar{\lambda}_1}{\bar{\lambda}_2 - \bar{\lambda}_1} (\exp(-\bar{\lambda}_1 \bar{t}) - \exp(-\bar{\lambda}_2 \bar{t})) \frac{\sqrt{\bar{\lambda}}}{\sqrt{4\pi(\bar{t}-1)^3}} \exp\left[-\frac{\bar{\lambda}}{4(\bar{t}-1)}\right], \end{aligned} \quad (6.67b)$$

where C_1^i and C_2^i are concentrations of the parent and daughter components with an impulse input function, $\bar{t} = \frac{t}{t_0} = \frac{u}{x}$, $\bar{\lambda} = B_m t_0$, $\bar{\lambda}_i = \lambda_i t_0$, $B_m = \sigma^2 \lambda_m$ is a bed with uniformly distributed fractures and with averaged mass exchange coefficient λ_m (6.11), $B_m = D_m \phi_m^2 / b_f^2$ is a unit fracture with aperture of $2b_f$ in a porous massif.

From equations (6.67a) and (6.67b), it follows that the concentration ratios of parent to daughter components

$$\bar{C}_{21}^i = \frac{\bar{C}_2^i}{\bar{C}_1^i} = \frac{\lambda_1}{\lambda_2 - \lambda_1} \frac{e^{-\lambda_1 t} - e^{-\lambda_2 t}}{e^{-\lambda_1 t}} \quad (6.68)$$

do not depend on porous-matrix parameters. Specifically, with $\lambda_2 = 0$ we come to the well-known model used to date groundwater by $^3\text{H}/^3\text{He}$ -method (see Sect. 3.3.2). Estimates of the ratio $\bar{C}_{21}^i$ ($[^3\text{He}]/[^3\text{H}]$) in an aquifer makes it possible to evaluate the time $t = t_0 = x/u$, corresponding to groundwater age, i.e., the time between the entry of a tritium *impulse* into an aquifer and the moment of its record in the observation point x .

The solution proposed for a horizontal impulse can be generalized to the case of constant boundary concentration. In accordance with (1.122), we have:

$$\bar{C}_{1,2}(\bar{t}) = \int_1^{\bar{t}} \bar{C}_{1,2}^i(\tau) d\tau. \quad (6.69)$$

The plots of solutions (6.67a), (6.67b), and (6.69) in Figs. 6.7 and 6.8 illustrate the behavior features of concentration functions. The calculated curves (1 and 2), considering the standardization of coefficients $\bar{\lambda}$ and $\bar{\lambda}_i$ with respect to time t_0 , differ

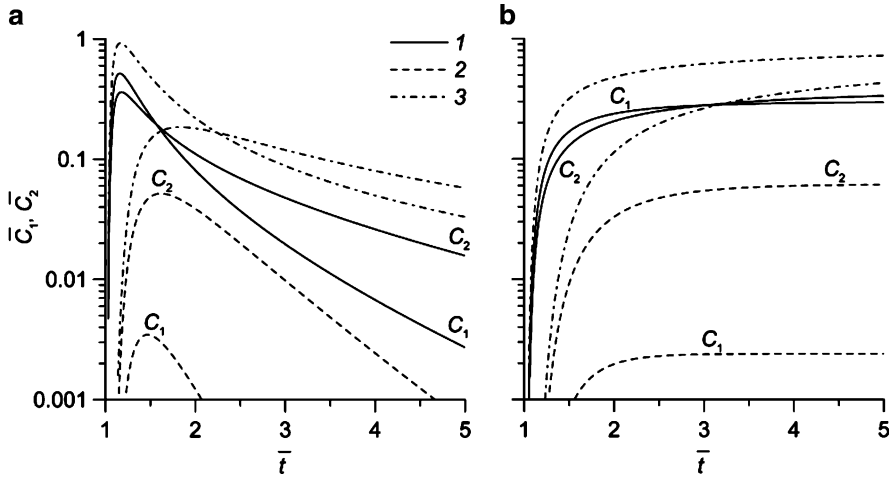


Fig. 6.7 Two-member decay chain: (a) impulse and (b) step-wise input functions. (1) $\bar{\lambda} = 1$, $\bar{\lambda}_1 = 0.5$, $\bar{\lambda}_2 = 0.2$; (2) $\bar{\lambda} = 5$, $\bar{\lambda}_1 = 2.5$, $\bar{\lambda}_2 = 1$; (3) transport of stable ($\bar{\lambda}_1 = \bar{\lambda}_2 = 0$) component

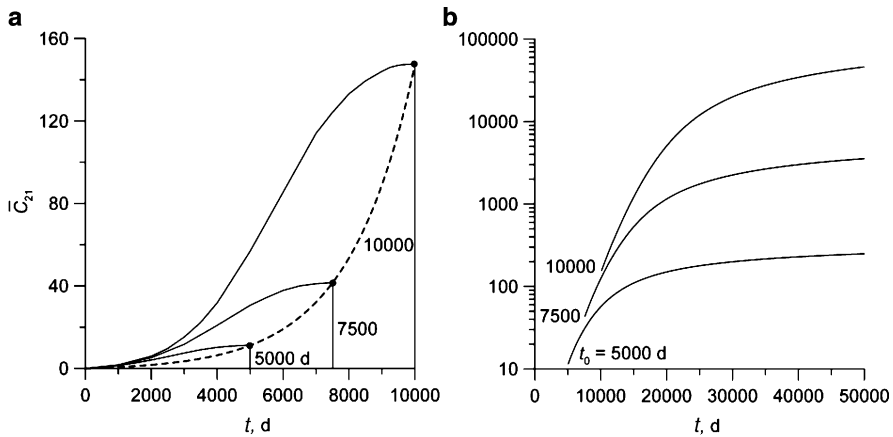


Fig. 6.8 (a) Concentration profiles $\bar{C}_{21} = f(x/u)$ for different time moments and (b) plots of $\bar{C}_{21} = f(t)$ in points $x = ut_0$. The dashed line is for the case of a single porosity aquifer. $B_m = 10^{-3} d^{-1}$, $\lambda_1 = 5 \times 10^{-4} d^{-1}$, $\lambda_2 = 0$

by the spatial position of the concentration record points $\bar{C}_1^i$ and $\bar{C}_2^i$ ($\bar{C}_1$ and $\bar{C}_2$). One can easily see that the downstream displacement of point x is accompanied by almost complete disappearance (in this example) of the parent component and the domination in water of its decay products.

Analysis of solution (6.69) shows that, with a step-wise input signal, the ratio $\bar{C}_2(t)/\bar{C}_1(t)$ differs from the respective ratio calculated by (6.68). A characteristic feature of the available solutions, describing the migration of unstable components in homogeneous single-porosity systems, is the formation of stationary

concentration distributions behind the piston-like displacement front ($t \geq t_0$). This is not the case in dual-porosity systems (Fig. 6.8a): the kinetics of diffusion solute exchange between the permeable and impermeable elements determines the nonstationary character of concentration function at the trailing edge, i.e., the concentrations continue growing after the front passes any point in the flow. As can be seen from the plot (Fig. 6.8a), the concentrations are equal to the values determined by solutions for a homogenous aquifer only in the moment when the concentration wave reaches this point. In particular, in this moment, the concentration ratio is exactly the same as determined by the solution (6.68), which is fundamental for the interpretation of data in studying the distribution of the isotopic pair $^3\text{H}/^3\text{He}$. Clearly, when used in the general case, it will overestimate the age of groundwater (when correlated with the time of particle motion in fractures), since the ratio $\bar{C}_2(t)/\bar{C}_1(t)$ will be always greater than the stationary values in an equivalent homogeneous bed (where the diffusion-based solute exchange between fractures and blocks is insignificant).

For an input signal $C_0(t)$ with arbitrary shape, we can write

$$C_{1,2}(\bar{t}) = \int_0^{\bar{t}} C_0(\bar{t} - \tau) \bar{C}_{1,2}^i(\tau) d\tau. \quad (6.70)$$

In principle, this solution can serve as a base for the transformation of the global tritium function (Sect. 3.4.2, Fig. 3.9), so that the interpretation capacity of $^3\text{H}/^3\text{He}$ -method can be extended.

In the above analysis we have assumed that porous matrix has unlimited diffusion capacity. It is clear, however, that the major conclusion will not change qualitatively when we consider matrix diffusion time scales corresponding to the first-order mass transfer model (Neumann et al. 2008). In particular, simulations of tritium and helium-3 transport and diffusive mass transfer showed that mass transfer can shift the $^3\text{H}/^3\text{He}$ age of the tritium and helium-3 concentration ($^3\text{H} + ^3\text{He}$) peak to dates much younger than the observed 1963 peak in atmospheric tritium (Sect. 3.4.2).

In general, $^3\text{H}/^3\text{He}$ data provide information about mass-transfer processes in dual porosity systems that can be used to constrain mass-transfer models.

In conclusion, we discuss in brief the space and time extent of the applicability of the limiting models considered here. Obviously, the presence of decay (destruction) in porous matrix radically extends the applicability range of the unlimited capacity scheme (as compared with the lumped capacity scheme), because this process reduces the saturation degree of porous blocks with the solute. When the tentative criterion is met

$$S_b^2 D_m / \lambda < 0.25 - 0.5, \quad (6.71)$$

this scheme has a practically unlimited application, since the stationary concentration distribution that forms in porous blocks embraces only their near-surface domain. In the case of a well-absorbable components, when the capacity of the porous matrix is controlled by $R_m = 1 + K_d \rho_b / \phi_m$, the competitive ability of the unlimited-capacity model is even greater.

6.4.3 Migration of Unstable Components Under Areal Recharge

The situation under consideration corresponds to the conceptual scheme presented in Fig. 3.1a. One-dimensional groundwater motion is assumed to exist in the fractured-porous aquifer under the effect of water input with the specific discharge, Q_0 , at the boundary of the bed ($x = 0$) and the area-distributed infiltration of atmospheric water with the specific rate of ε .

Let us construct an governing differential equation, assuming that the entire kinetic of the process is determined by the destruction of components, diffusing within the porous matrix, while the capacity of fractures can be neglected ($\phi \ll \phi_m$):

$$(Q_0 + \varepsilon x) \frac{\partial C}{\partial x} + \varepsilon C + W_{sr} \phi_m m = \varepsilon C_R; \quad (6.72)$$

$$W_{sr} = \sqrt{\lambda_m} \frac{\partial}{\partial t} \int_0^t e^{-\lambda \tau} \frac{C d\tau}{\sqrt{\pi(t-\tau)}} \quad (6.72a)$$

is the specific mass flux from fractures into blocks, $\lambda_m = S_b^2 D_m$, C_R is solute concentration in the infiltration water, τ is a variable of integration.

The expression (6.72a) for function W_{sr} corresponds to the assumption that the capacity of porous blocks is unlimited: the saturation of blocks by the solute decaying in them is far from completion at the moment when solute concentration distribution becomes stationary. This will surely take place when condition (6.71) is satisfied.

The solution of (6.72) in Laplace transforms is

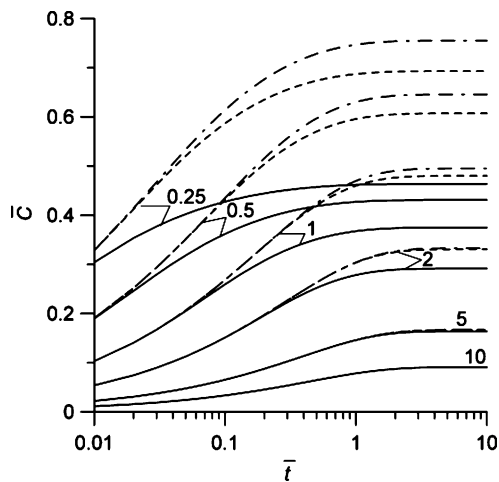
$$\frac{\tilde{C}}{C_R} = \frac{1}{p(1 + \alpha\sqrt{p+\bar{\lambda}})} - \frac{1}{p(1 + \alpha\sqrt{p+\bar{\lambda}})} V^{-(1-\alpha\sqrt{p+\bar{\lambda}})}, \quad (6.73)$$

where $\alpha = \sqrt{\lambda_m} m \phi_m / \varepsilon$, $V = 1 + \varepsilon x / Q_0$. The inverse transform yields the following expression for the dimensionless concentration:

$$\begin{aligned} \bar{C} = & \frac{1}{1+r} + \frac{1}{1-r^2} \left\{ r \operatorname{erfc}(\sqrt{\bar{t}}) - e^{\frac{r}{2}(1-r^2)} \left[\operatorname{erfc}\left(\frac{\sqrt{\bar{t}}}{r}\right) - \operatorname{erfc}\left(\frac{r \ln V}{2\sqrt{\bar{t}}} + \frac{\sqrt{\bar{t}}}{r}\right) \right] \right\} \\ & - \frac{1}{2} \left[\frac{e^{-(1+r) \ln V}}{1+r} \operatorname{erfc}\left(\frac{r \ln V}{2\sqrt{\bar{t}}} - \sqrt{\bar{t}}\right) + \frac{e^{-(1-r) \ln V}}{1-r} \operatorname{erfc}\left(\frac{r \ln V}{2\sqrt{\bar{t}}} + \sqrt{\bar{t}}\right) \right], \quad (6.74) \end{aligned}$$

where $\bar{t} = \lambda t$, $r = \sqrt{\lambda_m \bar{\lambda}} m \phi_m / \varepsilon$, $\bar{C} = C / C_R$.

Fig. 6.9 Plots of solution (6.74). Full lines are for $V = 2$, dashed lines for $V = 5$, and dash-and-dot lines are for $V = 10$. Figures at the curves are the values of parameter r



Some special cases of solution (6.80), plotted in Fig. 6.9, include

$$\text{at } r \rightarrow 0, \quad \bar{C} = 1 - 1/V, \quad (6.75a)$$

$$\text{at } V \rightarrow \infty, \quad \bar{C} = 1 + 1/(1+r), \quad (6.75b)$$

$$\text{at } \bar{t} \rightarrow \infty, \quad \bar{C} = \left[1 - V^{-(1+r)} \right] / (1+r). \quad (6.75c)$$

The latter asymptotics, corresponding to a stationary distribution, is attained, practically, at $\bar{t} = \lambda t > 2 \div 3$.

The relationship for the stationary phase of the process, taking into account fracture capacity, has the form similar to (6.75c):

$$\bar{C} = \frac{1}{1+r+\lambda_\varepsilon} \left[1 - V^{-(1+r+\lambda_\varepsilon)} \right], \quad (6.76)$$

where $\lambda_\varepsilon = \lambda m \phi / \varepsilon$. The solution (3.20) obtained before can be seen to be a specific case of (6.76): assuming in the latter $\lambda_m = 0$ ($r = 0$), we come to the description of mass transfer in a single porosity aquifer. From here, one can readily find the criterion of significance of decay reactions taking place in porous blocks:

$$r(1+\lambda_\varepsilon)^{-1} < 0.05 \div 0.1. \quad (6.77a)$$

When two criterions

$$\alpha_m t > 10 \text{ and } \alpha_m \lambda^{-1} > 10 \quad (6.77b)$$

are met simultaneously, the limiting macrodispersion calculation scheme is applicable. The relationships (6.77b) correspond to the condition of sufficiently complete

saturation of porous blocks by the solute, which in this case has not enough time to appreciably decay during its diffusion from the periphery to the center of the rock block. In such case, ϕ in all basic solutions can be replaced by $\phi + \phi_m \approx \phi_m$.

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Chapter 7

Flow and Transport Through Unsaturated Fractured-Porous Rocks

7.1 Problem Conceptualization

The models discussed in the previous chapter can potentially be expanded to study hydrological processes in the unsaturated zone presented by fractured formations. The *dual porosity* models are of primary interest for describing infiltration and solute transport. In these models the matrix acts as a source or sinks for *water imbibition* and dissolved component *diffusion* between the adjacent fractures, and it is more often assumed that solutes cannot move globally through matrix by advection. However analysis of flow and transport in partially saturated media may require incorporating a *dual porosity–dual permeability* modeling concept. In the dual permeability matrix diffusion models, the solute can transport globally through matrix by advection as well as diffusion (Gerke and van Genuchten 1993a; Ho 2001a, b; Mathias et al. 2005; Gerke 2006a, b; Houseworth 2006).

The models are distinguished depending on the character and space–time manifestation scale of molecular forces determining the interface capillary pressure at the interface between porous blocks and fractures, as well as on the conditions on the horizontal boundaries of the aeration zone, i.e., the daylight surface and phreatic-water table. Migration of water and solutes in the unsaturated fractured-porous systems depends on recharge condition.

Thus, in some natural situations, groundwater infiltration recharge weakly varies within the year, and the processes of water seepage and dissolved solute transport are nearly steady-state. The same is true for the case when the effect of climatic (seasonal) cycles of water input into the aeration zone is largely smoothed owing to the long periods of water movement in aerated rocks with a large thickness (which is equivalent to the condition $t_a \gg t_c$, where t_a is the characteristic time of moisture front movement from the surface to groundwater table, t_c is the period of seasonal cycles). Moisture profile is also steady in such cases. A characteristic feature of stationarity is the equality of capillary pressures in fractures and porous blocks, a feature that can be defined as the *local equilibrium* between two continua.

Other models belong to the unsteady-state (or, in a wider sense, nonequilibrium) type. Their construction is associated with the need to describe moving moisture fronts. Such fronts form, for example, when there are powerful artificial sources of additional infiltration groundwater recharge on land surface, or when short-time

higher intensity precipitation events create the conditions for rapid movement (often focused in individual channels) of moisture parcels from land surface to groundwater table. Such regime involves unsteady moisture exchange between porous matrix and fractures, and the process as a whole is *nonequilibrium* (Gerke 2006b; Jarvis 2007).

In such cases the time within which capillary pressures in fractures and pores are different, is comparable with the time interval within which the infiltration process is analyzed. In other words, the water moving through high-permeability zones (fractures) has not enough time to come to equilibrium with the immovable or slowly moving water filling the porous matrix or retained in stagnant zones in it. The description of the infiltration process in nonequilibrium models is a very efficient approach, providing a quantitative base allowing one to explain the formation in the aeration zone of prevailing paths of fast fluid transport in structured media (macro-porous soils and fractured-porous rocks) (Pruess 1999; Šimůnek et al. 2003).

In general, one can conclude that the migration and retardation of solutes is strongly influenced by recharge conditions (Wang and Narasimhan 1985; Brouyère et al. 2005). Under intense-injection conditions occurring during the period of storm rainfall, solutes migrate at high speed along the partially saturated fissures and may quickly reach the saturated zone. At the same time, they are temporarily retarded in the almost immobile water located in the porous matrix. Under normal recharge conditions, fissures are inactive and solutes migrate slowly through the dual porosity system.

Figure 2.2 above, which correlates the moisture transfer coefficient and capillary pressure (suction height), as well as comments to it (see Sect. 2.1.1) provide some explanation to this phenomenon. The capillary pressure in this case can reach tens and even hundreds of meters. Thus, despite the fact that the hydraulic conductivity of completely saturated fractured medium is many times as large as that of porous blocks, groundwater flow in aerated state concentrates in the space between fractures, i.e., in pores.

Plots in Fig. 7.1 give an illustration. They show variations in the partial moisture transfer coefficients of fractures k_f and porous matrix k_m , determined by Eq. 2.12, as well as the effective moisture transfer coefficient k_e , which determines the steady (equilibrium) moisture transfer in the massif (see formula (7.2) below); α_f and α_m are the sorptive numbers for fractures and matrix. In particular, it can be seen that coefficient k_e at low rock moisture content (i.e., at high suction pressure $|\psi|$) is almost completely determined by the permeability of porous blocks. The curve $k_e(\psi)$ (Fig. 7.1a) contains two plateaus, where $k_e(\psi) \approx \text{const}$; variations in the values of $k_e(\psi)$ are very fast beyond their boundaries. The second plateau in the plot of $k_e(\psi)$ in Fig. 7.1b is not pronounced. Curves $k_e(\psi)$, similar to those given in Fig. 7.1, have been obtained by numerically solving Richards equation (see Sect. 2.1.2) for a model domain containing porous blocks and fractures (Eaton and Dykhuizen 1988).

The hydraulic interaction between the blocks, which ensures the continuity of flow in discrete fracture space (air-filled), takes place only in the points (zones) of contact between individual blocks, i.e., in pinches in the fracture space formed by rough surfaces. The vertical flow from one block to another is either achieved by

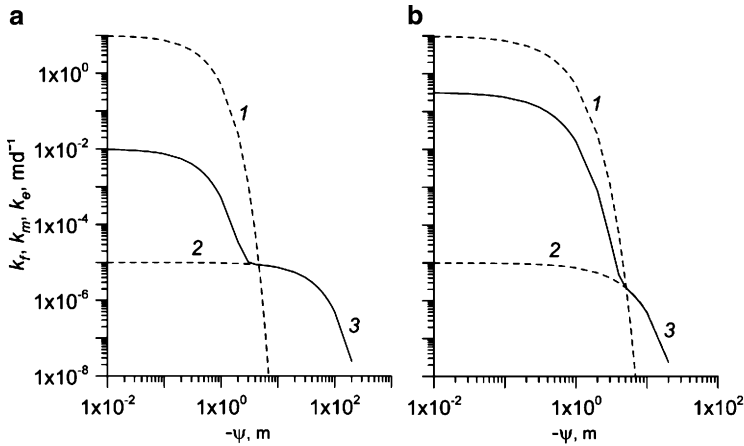


Fig. 7.1 Calculated moisture transfer coefficients (a) $\phi_f = 0.001$, $\alpha_m = 0.01 \text{ m}^{-1}$, (b) $\phi_f = 0.0323$, $\alpha_m = 0.1 \text{ m}^{-1}$. (1) k_f , (2) k_m , (3) k_e . $k_f^s = 10 \text{ md}^{-1}$, $k_m^s = 0.00001 \text{ md}^{-1}$, $\alpha_f = 1 \text{ m}^{-1}$, $n = 3$

(a) film flow across contact points or (b) by liquid bridges (Wang and Narasimhan 1985; Uleberg and Kleppe 1996; Neuman 2005; Carminati et al. 2008). This liquid transmissibility across the fracture is therefore an important parameter for calculating the rate of drainage of a stack of matrix blocks. The effective hydraulic conductivity coefficient of the medium k_e is always less than that of saturated porous matrix (k_{ms}) because of the imperfect interaction between blocks, as can be seen from conceptual numerical and analytical models (Mathias et al. 2005; Carminati et al. 2008).

Thus, moisture migration modeling in a completely saturated porous block with limited outlet cross-section area (F_c), corresponding to the contact area with the nearby (underlying) block, shows (Mathias et al. 2005), that with $F_c \approx 0.01 F_b$ (F_b is the total area of the horizontal surface of the block), the effective hydraulic conductivity k_e amounts to about 20% of the value of k_{ms} . With partial water saturation of pore blocks, the ratio $k_e(\psi)/k_m(\psi)$ can be as little as tenths or hundredths parts of percent, while the values of the capillary head $|\psi|$ are high (Carminati et al. 2008). It should be mentioned, however, that the small value of $k_e(\psi)/k_m(\psi)$ was obtained for a model where the matrix was represented by spherical porous agglomerates with relatively small contact area between them.

All of the above employs nothing more than a macroscale continuum concept assuming large-scale volume averaging for dual porosity–dual permeability media. Apart from this analysis remains widely used today discrete fracture network and stochastic continuum approaches that mentioned in the preface of Chap. 2. These approaches allow one to quantify preferential flow paths and flow-focusing behavior in heterogeneous fractured media. The answer to the question how may flow paths develop in the randomly described fracture network and what parameters control the flow-focusing phenomena in unsaturated zone presented by fractured rocks can be found in a number of qualified reviews (Pruess 1999; Liu et al. 2002; Zhang et al. 2004; Neuman 2005).

7.2 Saturation Profile at Steady-State

Since the vertical gradients of function ψ (the suction height or capillary head [L] < 0) in fractures and porous matrix are the same under steady-state infiltration regime, the following generalized expression holds for the total fluid flow (Peters and Klavetter 1988)

$$q = -k_e(\psi) \left(\frac{d\psi}{dz} + 1 \right), \quad (7.1)$$

similar to Darcy's formula (2.9), written for flow in "composite materials" where the *effective* moisture transfer coefficient is defined as (Ho 2001a, b)

$$k_e(\psi) = k_f(\psi)\phi_f + k_m(\psi)(1 - \phi_f); \quad (7.2)$$

where $k_f(\psi)$ and $k_m(\psi)$ are "partial" moisture transfer coefficients (hydraulic conductivities at incomplete saturation) in fractures and porous blocks [LT⁻¹]; hereafter, to unify denotations, we will use subscripts f and m for fractures and pores, respectively. The parameter ϕ_f characterizes the volume of water-bearing fractures, V_f , in a representative volume of rock, $V_f + V_m$, i.e., $\phi_f = V_f / (V_f + V_m)$, while ϕ_m is the ratio V_p / V_m (V_p is pore volume). Combining (7.1) and (7.2) yields

$$q = q_f\phi_f + q_m(1 - \phi_f), \quad (7.3)$$

where $q_f = q_f(\psi)$ and $q_m = q_m(\psi)$ are Darcy velocities in fractures and porous blocks (matrix).

Formula (7.1) can be transformed and integrated to correlate the increment of the capillary suction and the change in the current coordinate z :

$$z_i = z_{i-1} - \int_{\psi_{i-1}}^{\psi_i} \frac{d\psi}{1 + \frac{k_f(\psi)\phi_f + k_m(\psi)(1 - \phi_f)}{q}}, \quad (7.4)$$

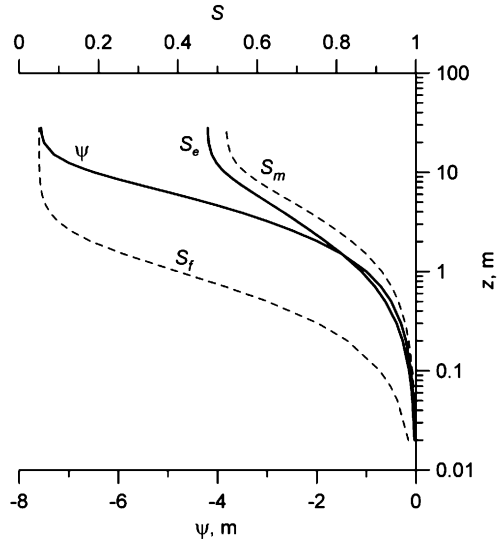
where $z = z_0 = 0$ ($i = 1$) is the elevation of groundwater table, and $\psi = \psi_0 = 0$; the coordinate z is measured upward, implying that $q < 0$.

The practical application of formula (7.4) and the construction of partial solutions for the distribution of water particle motion velocities in fractures and porous matrix requires evaluating the basic capillary characteristics, i.e., functional relationships between $S_{f,m}$ and $\psi - k_{f,m}$ (see Sect. 2.1.1). Once these relationships are established, the solution (7.4) allows the gradient of ψ to be found and moisture migration velocities to be calculated from the evident equalities:

$$u_f^w = \frac{q_f}{\theta_f - \theta_{rf}} = -\frac{k_f(\psi)}{S_f - S_{rf}} \left(\frac{d\psi}{dz} + 1 \right), \quad (7.5a)$$

$$u_m^w = \frac{q_m}{\theta_m - \theta_{rm}} = -\frac{k_m(\psi)}{\phi_m(S_m - S_{rm})} \left(\frac{d\psi}{dz} + 1 \right), \quad (7.5b)$$

Fig. 7.2 Suction pressure and saturation function versus depth. $q = 0.0001 \text{ md}^{-1}$, $\phi_f = 0.0323$, $\phi_m = 0.3$, $k_{fs} = 10 \text{ md}^{-1}$, $k_{ms} = 0.001 \text{ md}^{-1}$, $\alpha_f = 1 \text{ m}^{-1}$, $\alpha_m = 0.1 \text{ m}^{-1}$, $n_f = n_m = n = 3$, $S_{rf} = 0.05$, $S_{rm} = 0.1$



where $S_{f,m}$, $\theta_{f,m}$ are the saturation and moisture content ($S_f = \theta_f$, $S_m = \theta_m/\phi_m$), $S_{rf,m}$, $\theta_{rf,m}$ are the residual saturation and moisture content.

Calculations using the simplest exponential relationships proposed by Gardner (2.5) and Averyanov (2.10)

$$S_{f,m} = S_{rf,m} + (1 - S_{rf,m}) \exp(\alpha_{f,m} \psi), k_{f,m}(\psi) = k_{fs,ms} \exp(n \alpha_{f,m} \psi) (\psi < 0), \quad (7.6)$$

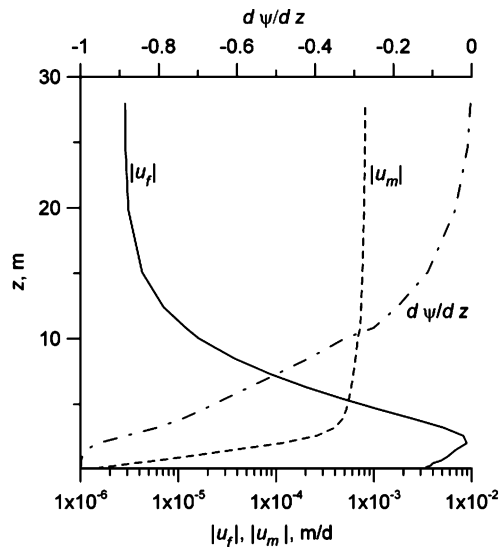
are plotted in Figs. 7.2 and 7.3; here $k_{fs,ms}$ is hydraulic conductivity at complete saturation; $\alpha_{f,m}$ and n are empirical coefficients (see Sect. 2.1.1). The curve of mean (effective) saturation of the medium (Fig. 7.1)

$$S_e = \frac{\theta_f V_f + \theta_m V_m}{V_f + V_p} = \frac{S_f \phi_f + S_m (1 - \phi_f) \phi_m}{\phi_f + (1 - \phi_f) \phi_m}. \quad (7.7)$$

reflects the total moisture content in a unit volume of void space in the rock (Ho 2001a, b). This specific example illustrates some general tendencies in the distribution and motion of moisture in a medium with dual porosity with $q < k_m$.

Thus, calculations show that the effective saturation S_e of fractured-porous medium decreases with the distance from groundwater table (Fig. 7.2). The plot shows that the saturation S_e at $z > 1 \text{ m}$ is almost completely determined by the saturation of the porous matrix, S_m : $S_m \gg S_f \approx S_{rf}$. This is accompanied by an increase in capillary pressure, resulting in an increase in the absolute values of function $|\psi|$. With such relationship between saturation levels, the pore matrix becomes more permeable for water (see Fig. 7.1b); therefore, its particle velocities in the domain $z > 5 \text{ m}$ under equilibrium ($\psi_f = \psi_m = \psi$) is greater than the appropriate characteristic for flow in fractures (Fig. 7.3).

Fig. 7.3 Capillary pressure and moisture migration velocity in fractures and porous matrix versus depth. For parameter values see Fig. 7.2



Thus, the model considered supports the conclusion that matrix flow dominates in fractured-porous rocks under incomplete saturation. Similarly, it can be shown that higher infiltration rate (the case $q > k_m^s$) favors the formation of appreciable flow in the system of fractures as well.

7.3 Solute Transport Under Steady-State Moisture Distribution Condition

Infiltration flow concentration in the porous matrix ($q < k_m^s$) results in that dissolved components are transported mostly through the pore space. When passing from moisture transfer velocities to the velocities of dissolved solute migration, one should take into account the total moisture capacity of the rock: $u_m^s = q_m / \theta_m (< u_m^w)$.

In the more general case, when the flow velocities q_f and q_m are comparable (with $q > k_m^s$), solute exchange between the two continuums is of importance in studying the protective properties of the aeration zone, represented by fractured-porous rocks. When substantiating process model, we will assume that the velocities q_f and q_m are constant above the capillary fringe and mass exchange is governed by diffusion mechanism. Suppose that the solute transfer between the two domains (first-order mass transfer model) can be assumed quasi-steady. Now the basic system of equations, which, in addition to diffusion exchange, takes into account advection in the two continuums, becomes

$$\begin{aligned}\frac{\partial C_f}{\partial t} + u_f^w \frac{\partial C_f}{\partial z} + \sigma \alpha_m (C_f - C_m) &= 0, \\ \frac{\partial C_m}{\partial t} + u_m^w \frac{\partial C_m}{\partial z} - \alpha_m (C_f - C_m) &= 0,\end{aligned}\quad (7.8)$$

i.e., a model of the process in a medium with double porosity and permeability; here C_f and C_m are solute concentrations in fractures and porous blocks, respectively; $\sigma = \phi_m / \phi_f$; α_m is the mass transfer rate coefficient. The relationships between the transfer parameter α_m and the state variables of pore velocity and water content are discussed in a paper by [Mayer et al. \(2008\)](#).

This model is best justified for describing the process in a medium where moisture moves mostly through vertical fractures with an aperture of $2b_f$, spaced on the average $2a_m$ apart. In this, maximally simplified case, the approximate equality $\alpha_m = \omega D_m(\theta_m) / a_m^2$ holds ($\omega = 3$ is a geometric factor), $\sigma = a_m \phi_m / b_f$. With $u_m^w = 0$, (7.8) degenerates into the conventional lumped capacitance model (see Sect. 6.1.2.3).

The boundary conditions have the form

$$C_f(z, 0) = C_m(z, 0) = 0, \quad C_f(\infty, t) = C_m(\infty, t) = 0, \quad C_f(0, t) = C_m(0, t) = \delta(t). \quad (7.9)$$

The latter condition reflects the impulse character of the input concentration function. The Eq. 7.8 can be reduced to the dimensionless form ([Barker et al. 2000](#); [Mathias et al. 2005](#))

$$\begin{aligned}\frac{\partial C_f}{\partial \tau} + \frac{(1 + \sigma)}{(1 + \beta \sigma)} \frac{\partial C_f}{\partial \eta} + \sigma \alpha (C_f - C_m) &= 0, \\ \frac{\partial C_m}{\partial \tau} + \beta \frac{(1 + \sigma)}{(1 + \beta \sigma)} \frac{\partial C_m}{\partial \eta} - \alpha (C_f - C_m) &= 0;\end{aligned}\quad (7.10)$$

the boundary conditions can be transformed in a similar manner; here

$$\tau = \frac{t}{t_a}, \quad \alpha = \alpha_m t_a, \quad t_a = \frac{L}{u_f^w} \frac{(1 + \sigma)}{(1 + \beta \sigma)}, \quad \beta = \frac{u_m^w}{u_f^w}, \quad \eta = \frac{z}{L}, \quad (7.10a)$$

L is the characteristic length in the direction of transport, t_a is the characteristic time of advection in fractures.

The solution of the problem in Laplace transforms was obtained in the form ([Mathias et al. 2005](#))

$$\tilde{C}_f(\eta, p) = \exp \left[-\frac{\eta}{2\beta} \frac{(1 + \beta \sigma)}{(1 + \sigma)} \left(A_1 - A_2^{1/2} \right) \right] + \exp \left[-\frac{\eta}{2\beta} \frac{(1 + \beta \sigma)}{(1 + \sigma)} \left(A_1 + A_2^{1/2} \right) \right], \quad (7.11)$$

where $A_1 = p(1 + \beta) + \alpha(1 + \beta\sigma)$, $A_2 = (1 + \beta\sigma)^2\alpha^2 + 2\alpha p(1 - \beta\sigma)(1 - \beta) + (1 - \beta)^2p^2$, p is a dimensionless (standardized with respect to t_d) parameter of Laplace transform.

The inverse transform can be made numerically. Numerical calculations show that an increase in β causes an increase in the maximal (peak) concentration values in fractures and accelerates the movement of the concentration wave. Physically, it can be explained by a drop in the intensity of diffusion exchange between fractures and pores during the advective filling of the latter by the solute (in the process of downward water movement).

7.4 Nonequilibrium Flow and Transport Processes

The propagation of contaminated water through partially saturated fractures and fracture networks includes interactions with porous matrix due to capillary imbibition and diffusion. Physical nonequilibrium occurs due to the presence of the gradient of capillary pressure at the fracture/matrix interface. This gradient provides unsteady state mass (water and solutes) transfer between mobile, flowing water in fractures and the immobile water in matrix (Fig. 7.4).

Interaction of the downward fluid flux with low permeability matrix determines the buffer (protective) properties of the unsaturated zone presented by fractured-porous formations or structured porous soils and, eventually, specifies the pollution-affected area and the intensity of pollution penetration under the groundwater table.

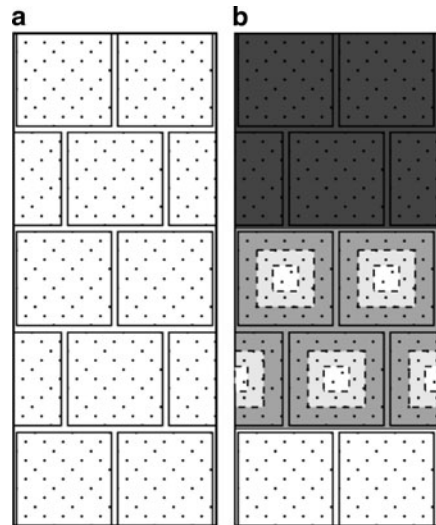


Fig. 7.4 Schematic diagram representing a dual porosity medium. (a) The initial distribution of saturation, (b) flow through fractures accompanying capillary imbibition and diffusion of solutes from fractures into rock matrix

7.4.1 Model-Based Approaches

The coupled water flow and solute transport in variable saturated fractured-porous formation is usually described using a system of flow and transport equations which are coupled by means of *first-order* expressions for two sink/source terms, capillary-controlled imbibition, W_w , and molecular diffusion, W_s (Gerke and van Genuchten 1993a, b, 1996; Šimůnek et al. 2003; Gerke 2006b). As an alternative to such approach, one- or two-dimensional *geometry-based diffusion models* may be used to simulate flow and mass transfer into and out of porous blocks of defined shapes (Gerke and van Genuchten 1996). The description of transient water movement in unsaturated fractured-porous systems is usually based on the solution of the *Richards equation*. On the other hand, conceptual framework for flow and solute transport in the two overlapping regions can be derived also from basic *kinematic wave theory* as it was suggested by Germann (1985) and Germann and Beven (1985), who used a kinematic wave equation to describe gravitational movement of water in macropores.

For one-dimensional vertical water flow in partially saturated fractures surrounded by porous matrix, a transfer rate function, W_w , is included in the conservation equation as follows

$$\frac{\partial \theta_f}{\partial t} + \frac{\partial q_f}{\partial z} + W_w = 0, \quad (7.12)$$

where θ_f is the soil water content stored in fractures; specific discharge, q_f , is determined by Darcy's law (2.9)

$$q_f = -k(\psi_f) \left(\frac{\partial \psi_f}{\partial z} + 1 \right). \quad (7.12a)$$

The construction of closed analytical solutions implies the introduction of some simplifications into the initial formulation of the problem. One of such simplification in studying infiltration problem is the assumption that the role of suction pressure (7.12) on the water front in fractures is insignificant ($\partial \psi_f / \partial z = 0$). In this case, water flux in the fractures is calculated with an approach derived from Darcy's law assuming a unit hydraulic gradient. Using a simple power law function (2.10) to present the unsaturated hydraulic conductivity, one may obtain from (7.12)

$$\frac{\partial \bar{\theta}}{\partial t} + \bar{k} n \bar{\theta}^{n-1} \frac{\partial \bar{\theta}}{\partial z} + \frac{W_w}{\phi_f} = 0, \quad (7.13)$$

where $\bar{\theta} = \theta_f / \phi_f$, $\bar{k} = k_{fs} / \phi_f$, k_{fs} is the saturated hydraulic conductivity of fractures; with such form of equation, function $\bar{\theta}$ is an analogue of saturation, S . We assume that the residual water content in the fracture domain is zero.

The dual porosity formulation for solute transport is based on the traditional convection-dispersion equation as follows

$$\frac{\partial(\theta_f C_f)}{\partial t} - \frac{\partial}{\partial z} \left(D_f \theta_f \frac{\partial C_f}{\partial z} - q_f C_f \right) + W_s = 0, \quad (7.14)$$

where C_f is the solute concentration in flowing solution.

The mass transfer and exchange between the domains is often approximated by first-order rate expressions. The implementation of these expressions for transfer terms utilizes average water content, θ_m , and average solute concentration, C_m , in porous matrix region

$$\frac{\partial \theta_m}{\partial t} = W_w, \quad \frac{\partial(\theta_m C_m)}{\partial t} = W_s. \quad (7.15)$$

Various approaches for modeling the mass transfer rate in (7.15) for water, W_w , between the fracture and matrix regions in dual porosity studies are discussed in numbers of publications (e.g., Jarvis and Larsson 2001; Šimůnek et al. 2003; Gerke 2006b; Šimůnek and van Genuchten 2008). The term W_w in different mass transfer formulations is assumed to be proportional to the difference in pressure head, effective saturation, and water content of the two regions using a first-order rate equation. A transfer function is included as a source/sink term in the one-dimensional conservation equation for each streamline as part of the solution of the mass transport problem.

Thus, in the frequently used MACRO simulator (Jarvis 1994; Jarvis and Larsson 2001; Gerke 2006b), water flow between the two regions is described with a modified (Gerke and van Genuchten 1993b) quasi-empirical equation using water saturation as a driving force for the exchange process

$$W_w = \frac{\partial \theta_m}{\partial t} = \frac{\omega D_w \gamma_w}{a_m^2} (\theta_b - \theta_m). \quad (7.16)$$

In this model the boundary between the two domains is defined by the air-entry pressure in the Brooks and Corey Eq. 2.11 with equivalent water content, θ_b , and hydraulic conductivity, k_b , defining the saturated state of porous matrix (Jarvis and Larsson 2001); here D_w is the effective soil water diffusivity (Jarvis 1994), which depends on the water diffusivity at the boundary (domains interface), current matrix water content; the term D_w includes also a multiplier, S_{fe} , the degree of saturation in macropores (fractures) to account for the effects of incomplete wetted contact area between the two domains; a_m is an effective diffusion pathlength, the characteristic length of the aggregate (e.g. the radius of a spherical aggregate, or half the fracture spacing for a parallel rectangular system); ω is a shape factor that depends on the geometry; for porous blocks of a rectangular slab geometry, $\omega = 3$ (Jarvis 1994; Jarvis and Larsson 2001); γ_w is a scaling factor, introduced to match approximate and exact solutions to the diffusion problem.

The transfer rate for solutes between the fracture and matrix domains, W_s , is usually given as the sum of diffusive and convective fluxes (Jarvis 1994; Gerke and van Genuchten 1996; Šimůnek et al. 2003; Larsbo et al. 2005; Gerke 2006b; Šimůnek and van Genuchten 2008)

$$W_s = \alpha_m \theta_m (C_f - C_m) + W_w C^*, \quad (7.17)$$

where $C^* = C_f$ at $W_w > 0$ and $C^* = C_m$ at $W_w < 0$; $\alpha_m = \omega D_m(\theta_m)/a_m^2$ is the effective fracture-matrix solute exchange coefficient; $D_m(\theta_m)$ is the pore diffusion coefficient; the term α_m can include a multiplier, S_{fe} , to account for the effects of incomplete wetted contact area between the two domains (Alaoui et al. 2003). Formally, if the mass transfer rate can be characterized by a characteristic diffusion path length, the mass transfer rate should increase with decreasing matrix water content (Mayer et al. 2008).

Considering the nonlinear character of the model (7.12)–(7.17), the hydrogeological interpretation of field material and forecasting required the use of mathematical modeling (Jarvis 1994; Šimůnek et al. 2003; Larsbo et al. 2005; Mathias 2005; Van den Daele et al. 2007). Some physical features of infiltration of water containing dissolved components can be analyzed under simplified model assumptions.

7.4.2 A Solution Describing the Early Stage of Wetting Front Propagation

Let us assume that the early stage of capillary-controlled water imbibition by porous matrix is described by Philip's asymptotic solution for "horizontal infiltration" (2.43)/(2.44)

$$i(t) \equiv q_m = \frac{S(\theta_s, \theta^0)}{2\sqrt{t}}, \quad (7.18)$$

where $S(\theta_s, \theta^0) = \sqrt{2k_m h_m (\theta_s - \theta^0)}$ is the water sorptivity (2.89a). Let us write (7.18) as

$$q_m = \frac{\sqrt{D_{we}}}{\sqrt{\pi t}} (\theta_s - \theta^0), \quad (7.19)$$

where the expression for the coefficient of effective water diffusivity,

$$D_{we} = (\pi/4) S^2 / \Delta \theta^2, \quad \Delta \theta = \theta_s - \theta^0, \quad (7.20)$$

coincides with the estimate in (Philip 1955); k_m is the saturated hydraulic conductivity of porous matrix; h_m is the capillary head at the moistening front.

Then a formulation for the mass transfer term is as follows

$$W_w = S_b q_m = \frac{S_b \sqrt{D_{we}}}{\sqrt{\pi t}} (\theta_s - \theta^0), \quad (7.21a)$$

or

$$W_w = S_b q_m = \frac{S_b D_{we}}{l(t)} (\theta_s - \theta^0), \quad l^2(t) = \pi D_{we} t, \quad (7.21b)$$

where $l(t)$ is moisture penetration depth into the porous matrix (Fig. 7.4); $(\theta_s - \theta^0)/l(t)$ is the current moisture gradient; θ_s is moisture content at complete saturation of the porous matrix; θ^0 is the initial moisture content ($t = 0$).

We represent the system of Eqs. 7.13, 7.21 for the early stage of the infiltration (a linear case, $n = 1$) as

$$\frac{\partial \bar{\theta}}{\partial t} + \bar{k} \frac{\partial \bar{\theta}}{\partial z} = -\frac{\sigma S_b D_{we}}{l(z, t)}, \quad 0 < \bar{\theta} \leq 1, \quad (7.22a)$$

$$\frac{\partial l^2(z, t)}{\partial t} = \begin{cases} \pi D_{we}, & 0 < \bar{\theta} \leq 1, \\ 0, & \bar{\theta} = 0; \end{cases} \quad (7.22b)$$

here $\sigma = (\theta_s - \theta^0)/\phi_f$. The boundary conditions are

$$\bar{\theta}(z, 0) = 0, \quad l(z, 0) = 0. \quad (7.22c)$$

Solution of the system of partial differential Eq. 7.22 can be associated with a problem related to the determination of two unknown movable boundaries of saturation, i.e., wetting front in the fractures, $t = \xi(z)$, and wetting front in the rock matrix, $t = \ell(z)$ (Kosterin and Selin 2000). Clearly, the wetting front $t = \xi(z)$ should move with a decreasing velocity and lag behind the hypothetical migration front $t = z\phi_f/k_{fs}$ of solution not imbibed by porous blocks.

The solution of the second equation of the system, which serves as an auxiliary equation in the search for solution of the problem as a whole, can be obviously written as

$$l^2(z, t) = \pi D_{we} [t - \xi(z)], \quad t > \xi(z). \quad (7.23)$$

The expression in brackets indicates that the fluid flow from fractures into blocks forms only after the front, whose time coordinate is $t = \xi(z)$, has reached the point z .

The solution of the main partial differential Eq. 7.22a is sought for by the method of characteristics, implying that this equation is replaced by its equivalent in the form of the system of ordinary differential equations:

$$\frac{dt}{1} = \frac{dz}{\bar{k}} = \frac{d\bar{\theta}}{-\sigma S_b D_{we}/l(z, t)}, \quad (7.24)$$

The degree of saturation changes along characteristics according to the law determined by the solution of the second equation of the system (7.22b) written as

$$\frac{d\bar{\theta}}{dz} = -\frac{N}{l(z, t)}, \quad N = \sigma S_b D_{we}/\bar{k}. \quad (7.25)$$

Since the saturation varies from 1 to 0 along any characteristic, we can write the integral identity

$$N \int_0^z \frac{dz'}{l(z')} = 1, \quad (7.26)$$

where z is the coordinate of the saturation front, governed by the trajectory of the leading saturation front $t = \xi(z)$, and

$$l(z') = \sqrt{\pi D_{we}} \sqrt{\xi(z) - \xi(z') - (z - z')/u}. \quad (7.27)$$

Kosterin and Selin (2000) introduced a new function $y(z) = \xi(z) - z/\bar{k}$, reducing the integral identity (7.26) to Abel's integral equation

$$\int_0^z \frac{dz'}{\sqrt{y(z) - y(z')}} = \frac{\sqrt{\pi D_{we}}}{N}, \quad (7.28)$$

whose solution has the form

$$y = \left(\frac{\pi N}{2\sqrt{\pi D_{we}}} \right)^2 z^2. \quad (7.29)$$

Thus, we come to the equation

$$\xi(z) = \frac{z}{\bar{k}} + \frac{\pi \sigma^2 S_b^2 D_{we}}{4 \bar{k}^2} z^2, \quad (7.30)$$

describing the movement of the leading front of saturation (the time taking the front to reach depth z from the surface).

Multiplying the left and right parts of Eq. 7.30 by $S_b^2 D_{we}$, we transform the equation for determining the position of the saturation front at time $t = \xi(z)$ into the dimensionless form:

$$\xi(\eta) \equiv \tau_\xi = \eta + \frac{\pi \sigma^2}{4} \eta^2, \quad (7.31)$$

$$\eta = S_b^2 D_{we} t_0, \tau = S_b^2 D_{we} t, \tau_\xi = S_b^2 D_{we} \xi(z), \quad t_0 = z \phi_f / k_{fs}, \sigma = \Delta \theta / \phi_f. \quad (7.31a)$$

The expression for the propagation depth of the wetting front into the porous matrix can be written in the following explicit form

$$l(z, t) = \sqrt{\pi D_{we} \left[t - \frac{z}{\bar{k}} - \frac{\pi \sigma^2 S_b^2 D_{we}}{4 \bar{k}^2} z^2 \right]}. \quad (7.32)$$

Now the distribution of the relative water content in fractures can be found by integrating (7.25), (7.23) along characteristics

$$\bar{\theta} = 1 - \frac{2}{\pi} \operatorname{arctg} \frac{\sqrt{\pi} \sigma \eta}{2\sqrt{\tau - \xi(\eta)}}. \quad (7.33)$$

7.4.3 The Integral Mass Balance Approach

In the context of practical application of the models considered here, of greatest interest is the determination of the function $z(t)$, since it characterizes the propagation velocity of the wetting front (i.e., it reflects the buffer properties of the aeration zone). Therefore, it makes sense to consider one more method for analysis of infiltration process (Barenblatt et al. 1990).

Suppose that water enters fractured-porous rocks from the surface ($z = 0$) at constant rate $q = k_{fs}$, which determines infiltration at unit gradient. Since the liquid is spent only for saturating the fracture space and porous blocks, we can write the following balance equation:

$$qdt = k_{fs}dt = \phi_f \frac{\partial z(t)}{\partial t} dt + \left[\int_0^{z(t)} W_w(t - \xi(z)) dz \right] dt, \quad (7.34)$$

where $\xi(z)$ is the time required for the saturation front to reach the depth z .

The integral expression in formula (7.34), which determines the rate of changes in the imbibition velocity, can be transformed by introducing a new integration variable $dz = [\partial z(\tau)/\partial \tau] d\tau$ into (Barenblatt et al. 1990)

$$\int_0^{z(t)} W_w[t - \xi(z)] dz = \int_0^t W_w(t - \tau) \frac{\partial z(\tau)}{\partial \tau} d\tau. \quad (7.35)$$

Thus, Eq. 7.34 becomes

$$k_{fs} = \phi_f \frac{\partial z(t)}{\partial t} + \int_0^t W_w(t - \tau) \frac{\partial z(\tau)}{\partial \tau} d\tau. \quad (7.36)$$

The integral expression in the balance equation is nothing else than a convolution integral, whose Laplace transform can be written as (see Sect. 1.3.3):

$$L \left[\int_0^t W_w(t - \tau) \frac{\partial z(\tau)}{\partial \tau} d\tau \right] = (\tilde{W}_w)(p\tilde{z}), \quad (7.37)$$

where $\tilde{W}_w = \tilde{W}_w(p)$ and $\tilde{z} = \tilde{z}(p)$ are the Laplace transforms of appropriate functions, p is transform parameter. The expression (7.37) is valid at zero initial conditions.

The Laplace transform of entire Eq. 7.34 becomes

$$\frac{k_{fs}}{p} = p \phi_f \tilde{z} + p \tilde{W}_w \tilde{z}. \quad (7.38)$$

The algebraic solution of Eq. 7.38 is

$$\tilde{z} = \frac{k_{fs}}{p^2 (\phi_f + \tilde{W}_w)}. \quad (7.39)$$

The Laplace transform of the source function (7.21a) is

$$\tilde{W}_w = \frac{S_b \sqrt{D_{we}}}{\sqrt{p}} \Delta \theta. \quad (7.40)$$

Substituting expression (7.40) for $\tilde{W}_w$ into the solution (7.39) yields

$$\tilde{z} = \frac{\bar{k}}{p^{3/2} (\sqrt{p} + \sigma S_b \sqrt{D_{we}})}. \quad (7.41)$$

Taking the inverse Laplace transform of function $\tilde{z}(p)$ with the help of tables (Bateman and Erdelyi 1954), we obtain

$$\sigma^2 \eta = \frac{2}{\sqrt{\pi}} \sigma \sqrt{\tau} + \exp(\sigma^2 \tau) \operatorname{erfc}(\sigma \sqrt{\tau}) - 1. \quad (7.42)$$

Calculations by formula (7.42) yield results similar to (7.31).

7.4.4 A Solution for Leading Front Propagation Under Exponentially Damped Regime of Water Imbibition into a Gas-Saturated Matrix Block

If the dual porosity model uses a first-order approximation for the mass transfer term (7.16), then at the later stage of the infiltration process (when $\theta_b \rightarrow \theta_s$) we can write a relationship

$$W_w = \frac{\partial \theta_m}{\partial t} \approx \frac{\omega D_w \gamma_w}{a_m^2} (\theta_s - \theta_m) \approx S_b^2 D_w (\theta_s - \theta_m). \quad (7.43)$$

The model (7.43) assumes that the water content driving force is governed by the difference between the saturated water content of micropores at the fracture-matrix interface, $\theta_s = \text{const}$, and water content of matrix $\theta_m = f(t)$. The formula (7.43)

is written for an idealistic case of infiltration through a porous medium, consisting of isometric porous blocks, whose all faces are assumed to be equally accessible for the liquid that fills the fracture space. For approximate estimates of conceptual character, we also assume that water diffusivity, D_w , remains constant over time, thus, $S_b^2 D_w = \lambda_w = \text{const}$ (effective coefficient of water exchange).

Let us analyze this regime of water imbibition by porous blocks by using integral balance method. With this in view, we write (7.43) as

$$\frac{\partial \bar{\theta}_m}{\partial t} = \lambda_w(1 - \bar{\theta}_m), \quad \bar{\theta}_m = (\theta_m - \theta^0)/(\theta_s - \theta^0), \quad (7.44)$$

Its solution:

$$\bar{\theta}_m = 1 - e^{-\lambda_w t}, \quad \partial \bar{\theta}_m / \partial t = \lambda_w e^{-\lambda_w t}, \quad \lambda_w = S_b^2 D_w. \quad (7.45)$$

Since $W_w \sim \partial \bar{\theta}_m / \partial t$, function W_w decays exponentially. Its Laplace transform is

$$\tilde{W}_w = \frac{\lambda_w \Delta \theta}{p + \lambda_w}, \quad \tilde{z} = \frac{\bar{k}(p + \lambda_w)}{p^2[p + \lambda_w(1 + \sigma)]}, \quad \sigma = \frac{\Delta \theta}{\Phi_f}, \quad \Delta \theta = \theta_s - \theta^0. \quad (7.46)$$

Taking inverse Laplace transform of (7.46) we obtain the solution

$$(1 + \sigma)^2 \eta = (1 + \sigma)\tau + \sigma[1 - \exp(-(1 + \sigma)\tau)], \quad (7.47)$$

which can be used for describing the motion of the wetting front at later stages of infiltration; here $\eta = S_b^2 D_w t_0$, $\tau = S_b^2 D_w t$, $t_0 = z/\bar{k}$.

7.4.5 A Generalized Solution

7.4.5.1 A New Form of the Sink/Source Function

The application ranges of the functional relationships for $\eta(\tau)$ (7.31), (7.42), and (7.47) have their own space and time scale. This is due to the limitations in the physical prerequisites in the formalization of mass transfer terms (7.21) and (7.43). The following approximation of mass transfer term (Skvortsov 1967; Kosterin and Skvortsov 2002) is free of such limitations

$$W_w(z, t) = \frac{A}{\sqrt{t - \xi(z)}} \exp[-B(t - \xi(z))] H(t - \xi(z)), \quad (7.48)$$

and has desirable asymptotics; here $H(t - \xi(z))$ is unit Heaviside function; A [$T^{-1/2}$] and B [T^{-1}] are formal kinetic coefficients. Coefficients A and B are to be determined from the analysis of system behavior under asymptotic regimes.

Thus, it is clear that with $t \rightarrow \xi(z)$, the terms W_w in formulas (7.48) and (7.21) must be identical. From here it follows

$$A = \frac{S_b \sqrt{D_{we} \Delta \theta^2}}{\sqrt{\pi}}. \quad (7.49)$$

To determine coefficient B , we consider solution of the problem (7.34)/(7.48) in Laplace transforms, which is given by formula (7.39) with $\tilde{W}_b = A\sqrt{\pi}/\sqrt{p+B}$ (Laplace transform of the source function (7.48)). Taking the inverse transform of (7.39) yields the following expression for the position of the front $\xi(z)$:

$$\frac{z}{k} = \frac{1}{A\sqrt{\pi B}} \left[\left(\frac{1}{2} + \alpha^2 \right) \operatorname{erf}(\alpha) + \frac{\alpha}{\sqrt{\pi}} \exp(-\alpha^2) \right], \quad (7.50)$$

which can be seen to be implicit with respect to $\xi(z)$. Here coefficient A is determined by (7.49), and

$$\alpha^2 = B \left[\xi(z) - \frac{z\phi_f}{k} \right]. \quad (7.51)$$

To find coefficient B , we introduce the condition

$$\xi(z) \rightarrow \frac{z}{k}(\phi_f + \Delta\theta) \text{ when } \alpha \rightarrow \infty. \quad (7.52)$$

It means that, when the exchange rate between fractures and blocks increases (or when the contact time is very long), the effective capacity of the system is governed by the available (full) storage capacity for saturation $\phi_f + \Delta\theta$. From here we have:

$$B = S_b^2 D_{we} = \frac{\pi A^2}{\Delta \theta^2}. \quad (7.53)$$

Now the full solution (7.50) can be represented in the dimensionless form

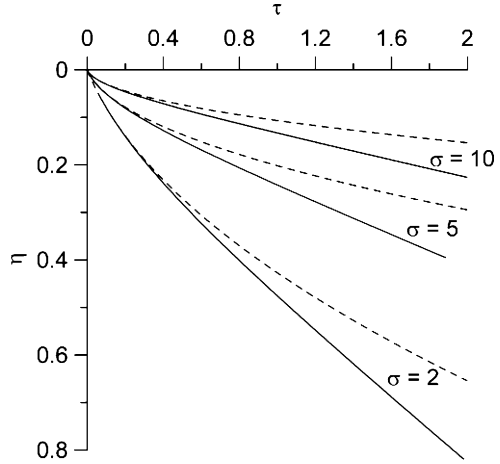
$$\sigma\eta = \left(\frac{1}{2} + \alpha^2 \right) \operatorname{erf}(\alpha) + \frac{\alpha}{\sqrt{\pi}} \exp(-\alpha^2), \quad \alpha^2 = (\tau_\xi - \eta), \quad (7.54)$$

where dimensionless groups τ_ξ , η , and σ are defined by (7.31a).

The solution (7.54) can be shown to meet all asymptotics considered above. Thus, at small α ($\alpha \rightarrow 0$), formula (7.54) takes the form $\sigma\eta = 2\alpha/\sqrt{\pi}$, corresponding to the solution (7.31). With small η , $\tau_\xi \approx \eta$ and the equation of motion of the front becomes $t = \xi(z) = \phi_f z/k_{fs}$, i.e., liquid migration rate is governed by the fracture capacity in the rock. With large α , we obtain $\sigma\eta = \alpha^2 = \tau_\xi(\eta) - \eta$, which yields the relationship (7.52), written for the characteristic $\xi(z)$ in an explicit form.

The results of calculation of function $\tau(\eta)$, shown in Fig. 7.5, provide an additional illustration for the features of the process mentioned above. Thus, it can be easily seen that the curves $\tau(\eta)$ calculated by (7.54) and (7.42) almost coincide

Fig. 7.5 Characteristic curves calculated (full lines) by (7.54) and (dashed lines) by (7.42)



at the initial stages of motion of the wetting front. For large times, the analysis of curves yields $d\tau/d\eta \approx 1 + \sigma$, suggesting that the fracture and pore spaces are almost completely filled by the liquid.

7.4.5.2 A Solution for Water Content Distribution Beneath the Surface

The full solution of the problem

$$\frac{\partial \bar{\theta}}{\partial t} + \bar{k} \frac{\partial \bar{\theta}}{\partial z} + \sigma \frac{S_b \sqrt{D_{we}}}{\sqrt{\pi(t - \xi(z))}} \exp[-S_b^2 D_{we}(t - \xi(z))] H(t - \xi(z)) = 0 \quad (7.55)$$

for a first-type boundary condition on the surface $\bar{\theta}(z = 0, t) = 1$ can be obtained by using Laplace transforms

$$\bar{\theta}(z, t) = \frac{\theta_f(z, t)}{\phi_f} = \frac{2}{\pi} \left[\exp(-\gamma^2) \arccos \frac{\alpha}{\gamma} + \pi^{1/2} \int_0^\beta \exp(-u^2) \operatorname{erf}(\gamma^2 - u^2)^{1/2} du \right], \quad (7.56)$$

where $\alpha^2 = \tau_\xi - \eta$, $\beta^2 = \tau - \tau_\xi$, $\gamma^2 = \tau - \eta$. The results of calculations by formula (7.56) are given in Figs. 7.6 and 7.7. Both plots are seen to have relatively sharp fronts of relative moisture content. The vertical displacement velocity of these fronts is governed by water diffusion from fractures into porous blocks under the effect of capillary forces. At long stages of water migration, $\eta \approx \tau/(1 + \sigma)$.

Moisture migration in a system of parallel vertical fractures separated by porous blocks is described by solution (7.56)–(7.54) with dimensionless parameters defined by

$$\eta = \alpha_{we} z \phi_f / k, \quad \tau = \alpha_{we} t, \quad \tau_\xi = \alpha_{we} \xi(z), \quad \alpha_{we} = D_{we} / a_m^2, \quad \sigma = \Delta \theta a_m / \phi_f b_f, \quad (7.57)$$

Fig. 7.6 Function $\bar{\theta}(\eta)$ with different values of τ (figures on curves), calculated by (7.56) for two particular values of dimensionless group σ

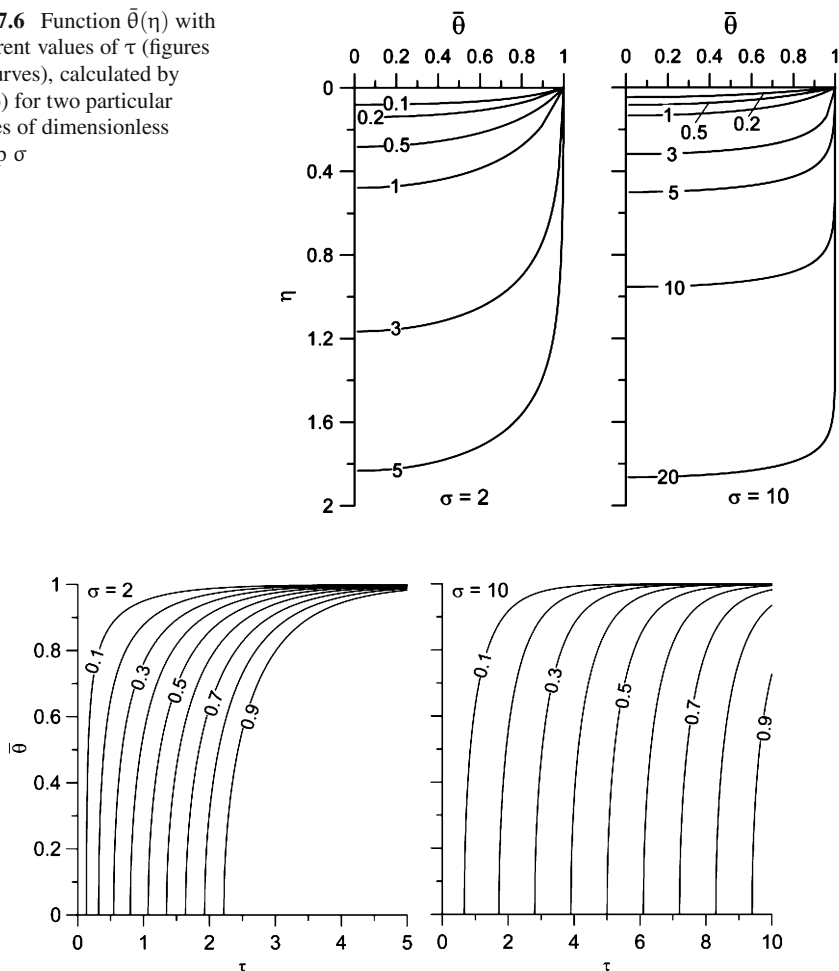


Fig. 7.7 Function $\bar{\theta}(\tau)$ with different values of η (figures on curves), calculated by (7.56) for two particular values of dimensionless group σ

where $2b_f$ and $2a_f$ are fracture opening and the horizontal distance between them, respectively; ϕ_f is the porosity of the disperse material filling fractures ($\phi_f = 1$ implies a “clear” fracture); k is the saturated hydraulic conductivity of the fracture; D_{we} is the effective water diffusivity (7.20).

Figure 7.8 illustrates the satisfactory agreement between calculations by (7.56) and the results of numerical modeling on program package TOUGH2 (EOS3). The basic parameters of the numerical model are as follows: $a_m = 0.0175$ m, $b_f = 5 \cdot 10^{-5}$ m, $q = k = 1$ md $^{-1}$, $\phi_f = 0.01$, $k_m = 1 \cdot 10^{-4}$ md $^{-1}$, $h_m = 0.1$ m. The calculation variants are (1) $\Delta\theta = 0.033$, $\alpha_{we} = 1.54$ d $^{-1}$ ($D_{we} = 4.72 \cdot 10^{-4}$ m ^{2} d $^{-1}$), $\sigma = 11.66$ (Fig. 7.8a); (2) $\Delta\theta = 0.066$, $\alpha_{we} = 0.77$ d $^{-1}$ ($D_{we} = 2.36 \cdot 10^{-4}$ m ^{2} d $^{-1}$), $\sigma = 23.32$ (Fig. 7.8b).

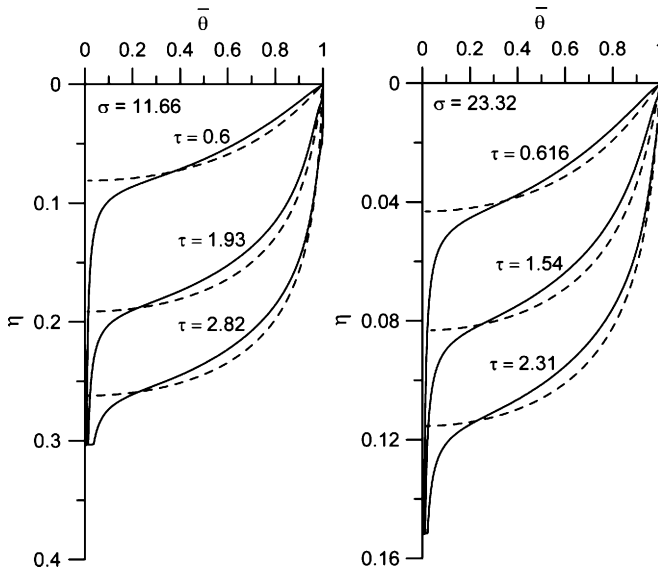


Fig. 7.8 Wetting front $\bar{\theta} = \bar{\theta}(\eta)$ at different dimensionless time, τ . A comparison of (dashed curves) analytical (7.56) and (full curves) modeling (TOUGH2) results

7.4.6 Kinematic Wave Approximation

7.4.6.1 A Conceptual Model

In all models discussed above, the transfer terms W_w were considered to be proportional to the specific surface of the matrix blocks: $W_w \sim S_b$. However it is obvious that in case of water infiltration in an unsaturated system, the wetted contact area between liquid in fractures and porous matrix must be less (due to flow localization in distinguished channels) than that defined by term S_b . This effect limits total imbibition rates to values less than saturated matrix hydraulic conductivity, leaving the rock matrix in partially saturated conditions even as water is flowing freely in portions of the fracture network (Pruess 1999). Intuitively one may presume that the effective specific area of fracture walls in contact with flowing liquid, S_{be} , is proportional to the effective saturation of the fracture region, $\bar{S}_f = \bar{\theta}$ (7.43). The effects of this type should be especially strong during the infiltration into relatively dry rocks when $\theta_m \ll \theta_s$. When these two assumptions are valid, the term W_w (7.43), which is responsible for the formalization of water exchange between fracture and matrix regions, can be presented as follows

$$W_w = S_b S_{be} D_w (\theta_s - \theta_m) \approx S_b^2 D_w \theta_s \bar{\theta}. \quad (7.58)$$

The continuity Eq. 7.12 in this case becomes

$$\frac{\partial \bar{\theta}}{\partial t} + \frac{\partial \bar{q}}{\partial z} + \sigma \lambda_w \bar{\theta} = 0, \quad (7.59)$$

$\bar{q} = q_f / \phi_f$, $\sigma = \theta_s / \phi_f$; $\lambda_w = S_b^2 D_w$ is the moisture imbibition coefficient [T^{-1}], an analogue of decay constant in mass transfer problems; $\bar{\theta} = \theta_f / \phi_f$.

Since the representation form of W_w in this analysis is implicitly associated with the manifestation of the channeling mechanism of water infiltration, to adequately describe the process, one has to consider strongly nonlinear functions $\bar{q} = f(\bar{\theta})$, e.g., Averjanov's power dependence (2.10):

$$\bar{q} = \bar{k} \bar{\theta}^n, \bar{k} = k_{fs} / \phi_f; \quad (7.60)$$

here, parameter $\bar{k}$ characterizes the conductivity of fracture [LT^{-1}]; the most likely value of parameter n (depending on the geometry of the fracture space, the initial moisture content, and the boundary condition) varies from 2 to 3, though it can come beyond this range; e.g., $n \gg 3$ when the jet flow in the fracture medium is very tortuous (Bendz et al. 1998).

The increase in n and decrease in S_{be} with decreasing water content, $\bar{\theta}$, is attributed to a significant increase in the tortuosity of the flow at the fracture networks scale (Tsang et al. 2000; Mayer et al. 2008).

In such formulation, Eq. 7.59 formally coincides with an equation which was suggested by Germann and Beven (1985) and Germann (1990) for describing gravitational movement of water in dual porosity system using a kinematic wave approach. Indeed, assuming

$$\frac{\partial \bar{\theta}}{\partial t} = \frac{d\bar{\theta}}{d\bar{q}} \frac{\partial \bar{q}}{\partial t} = \frac{1}{c} \frac{\partial \bar{q}}{\partial t}, \quad (7.61)$$

where

$$c = \frac{d\bar{q}}{d\bar{\theta}} = n \bar{k} \bar{\theta}^{n-1} = n \bar{k}^{1/n} \bar{q}^{(n-1)/n}, \quad (7.61a)$$

we can represent Eq. 7.59 in the form of kinematic wave equation (Germann and Beven 1985; Germann 1990; Bendz et al. 1998; Bendz and Singh 1999; Singh 2002):

$$\frac{\partial \bar{q}}{\partial t} + c \frac{\partial \bar{q}}{\partial z} + c \sigma \lambda_w \bar{\theta} = 0, \quad (7.62)$$

where parameter $c = c(\bar{q})$ [LT^{-1}] has the meaning of wave velocity (or celerity).

Equation 7.62 with substitutions (7.60) and (7.61a) becomes

$$\frac{\partial \bar{q}}{\partial t} + c(\bar{q}) \frac{\partial \bar{q}}{\partial z} = -n \sigma \lambda_w \bar{q}, \quad (7.63)$$

with an equivalent representation as a system of ordinary differential equations (see Sect. 1.2.1):

$$\frac{dt}{1} = \frac{dz}{c(\bar{q})} = -\frac{d\bar{q}}{n\sigma\lambda_w\bar{q}}. \quad (7.64)$$

The wetting front, within which moisture content varies from $\bar{\theta} = 0$ to $\bar{\theta} = \bar{\theta}_w$, moves downward with the velocity

$$c_w = \frac{\bar{q}}{\bar{\theta}_w} = \bar{k}^{1/n} \bar{q}^{(n-1)/n} = \bar{k} \bar{\theta}_w^{(n-1)}, \quad (7.65)$$

which is n times less than that of the wave front, c (7.61a).

7.4.6.2 Basic Characteristic Solutions

For a *square pulse of flux density input*, $\bar{q}_s$, at the surface, starting at $t = 0$ and ending at $t = t_s$ (Fig. 7.9), Germann and Beven (Germann and Beven 1985; Germann 1990) identify three characteristic regimes (stages) of infiltration.

The first stage involves the propagation of a leading wave, behind which steady moisture distribution establishes. Integrating Eq. 7.64 yields the expression describing the distribution of infiltration velocity over depth:

$$\bar{q}(z) = \bar{q}_s \left[1 - \frac{\sigma\lambda_w(a-1)}{c_s} z \right]^{n/(n-1)}, \quad (7.66)$$

where $c_s = d\bar{q}_s/d\bar{\theta} = n\bar{k}^{1/n}\bar{q}_s^{(n-1)/n}$. Obviously, there exists a limiting (maximal) depth of moisture penetration, z^* , which is due to the irreversible character of its losses from fractures during the saturation of porous matrix. From (7.66) it directly follows

$$z^* = \frac{c_s}{\sigma\lambda_w(n-1)}, \quad (7.67)$$

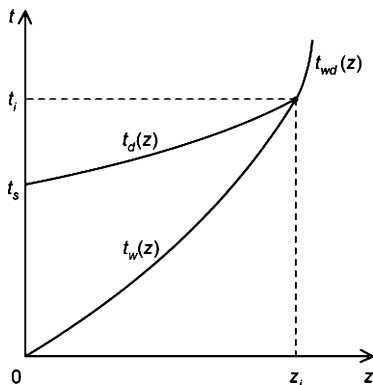


Fig. 7.9 Characteristic curves illustrating propagation and interaction of wetting and drained fronts

i.e., the greater the nonlinearity of the process, characterized by parameter n , the less the critical depth z^* . This yields another form of representation of function $\bar{q}(z)$ and an expression for moisture content profile:

$$\bar{q}(z) = \bar{q}_s(1 - z/z^*)^{n/(n-1)}, \quad \bar{\theta}(z) = \bar{\theta}_s(1 - z/z^*)^{1/(n-1)}, \quad (7.68)$$

where $\bar{\theta}_s = (\bar{q}_s/\bar{k})^{1/n}$, see Eq. 7.60.

According to (7.65) and considering (7.68), the velocity $c_w(z, t)$ of downward motion of the moisture front $z_w(t)$ can be described by

$$c_w(z) = (c_s/n)(1 - z/z^*) = dz_w/dt. \quad (7.69)$$

From here we obtain two major equations for characteristics of the wetting front (Fig. 7.9):

$$z_w(t) = [1 - \exp(-\sigma\lambda_w t(n-1)/n)]z^*, \quad (7.70a)$$

$$t_w(z) = -n/[\sigma\lambda_w(n-1)]\ln(1 - z/z^*). \quad (7.70b)$$

The second stage of the process involves the formation of the trailing edge (drainage front) of the moisture wave. At the moment t_s , when water input from the surface ceases, moisture content at this boundary falls to 0. The drainage front moves with the velocity

$$c_d(z) = c_s(1 - z/z^*) = dz_d/dt. \quad (7.71)$$

Integrating (7.71) yields two characteristic equations for the trailing edge

$$z_d(t) = [1 - \exp(-\sigma\lambda_w(t - t_s)(n-1))]z^*, \quad (7.72a)$$

$$t_d(z) = t_s - 1/[\sigma\lambda_w(n-1)]\ln(1 - z/z^*). \quad (7.72b)$$

The drainage front travels with velocity, c_d , which is greater than c_w (Fig. 7.9), thus at a certain time t_i at a depth z_i ,

$$t_i = t_s n/(n-1), \quad z_i = [1 - \exp(-\sigma\lambda_w t_s)]z^*, \quad (7.73)$$

the drainage front intercepts the wetting front.

An expression for moisture flux in fractures within the boundaries of the drainage wave can be found from (7.66) and (7.72) (considering (7.67)):

$$\bar{q}(z, t) = \frac{q(z, t)}{\phi_f} = \left[\frac{\sigma\lambda_w(n-1)z}{n\bar{k}^{1/a}(\exp[\sigma\lambda_w(t - t_s)(n-1)] - 1)} \right]^{n/(n-1)} \quad (7.74)$$

for $0 < z \leq z_d(t)$ and $t_s \leq t_d(z)$.

The third period is the dispersion of the wetting wave after the interaction between fronts. After the drainage front intercepts the wetting front, a single-crested function for depth $z > z_i$ evolves, and the water content of the peak begins to decrease (Germann 1990), so that the characteristic line $t_{wd}(z)$ becomes steeper (Fig. 7.9).

Overall, the model considered above provides adequate understanding of the character of motion of nonsteady moisture fronts in the aeration zone. The description of the process under the assumptions involved does not require one to know the parameters of any capillary (hydrophysical) function, thus making the model applicable to preliminary expert estimates in the absence of experimental data. The model neglects the capillary effects in fractures, simplifying the calculations.

7.4.7 Solute Transport Problem Formulation

Now we come to the description of migration problem. With this in view, neglecting dispersion in fractures, we write the continuity equation for the mass flux (7.14) in the form:

$$\frac{\partial(\bar{\theta}C_f)}{\partial t} + \frac{\partial(\bar{q}C_f)}{\partial z} + \frac{W_s}{\phi_f} = 0, \quad (7.75)$$

or (see Sect. 2.2.1), considering the continuity Eq. 7.12 for infiltration flow:

$$\bar{\theta} \frac{\partial C_f}{\partial t} + \bar{q} \frac{\partial C_f}{\partial z} - \frac{C_f W_w}{\phi_f} + \frac{W_s}{\phi_f} = 0. \quad (7.76)$$

Since the source terms are related by the equality (7.17), with $W_w > 0$ (when $C^* = C_f$), we come to the following equation:

$$\frac{\partial C_f}{\partial t} + \frac{\bar{q}}{\bar{\theta}} \frac{\partial C_f}{\partial z} = -\sigma \frac{\alpha_m \bar{\theta}_m}{\bar{\theta}} (C_f - C_m), \quad (7.77)$$

where $\sigma = (\theta_s - \theta^0)/\phi_f$, $\bar{\theta}_m = \theta_m/(\theta_s - \theta^0)$, $\bar{\theta} = \theta_f/\phi_f$. Equation 7.77 is a linear, first-order partial differential equation and can be solved along with balance Eq. 7.15 using a number of numerical techniques.

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Part III

Solute Transport Processes Induced by Recharge and Discharge Wells

The models discussed in the previous sections have focused mostly on the solute migration in flows whose planar structure was nearly one-dimensional and parallel while two-dimensional concentration profiles of dissolved species were controlled by a vertical component of flow velocity induced by area-distributed infiltration or stratification of aquifer properties. Models of this type, along with analyzed above quasi-one-dimensional transport models predicting averaged solute fluxes in dual porosity rock formations are clearly most appropriate for regional-scale estimates.

However, the redistribution of solutes in aquifers often has some features determined by perturbations in regional groundwater dynamics caused by the functioning of various sources of hydrodynamic disturbances. These include wells (or well systems), industrial waste retention basins, etc. In such cases, idealized, often unidirectional, streamline flow patterns can change radically, causing a kind of hydrodynamic deformation of the natural flow field. If the spatial extent of the process is local, as is the case during field well-tracer tests, one has to take into account the manifestations of hydrodynamic dispersion (microdispersion) effects, which are insignificant at the regional scale.

We are not going to give a comprehensive analysis of all computation situations of practical interest. The issue of migration flow formation in the zone of influence of hydrodynamic perturbation sources is the focus of vast literature. A large number of “standard” problems has been solved, describing the conditions of solute transport in the zone of influence of water intake or injection wells, as well as linear or area-distributed sources (sinks). A number of studies considered the effect of various hydrodynamic boundaries, either stabilizing or, conversely, facilitating the extension of contamination plumes. The solutions thus obtained form the basis, in particular, for the design substantiation of well-head protection zones for wellfields (groundwater supply systems), efficiency estimates of systems of in-situ remediation of contaminated groundwater, as well as deep injection disposal of hazardous and industrial waste and systems of in-situ leaching of ore (uranium, copper, gold, etc) deposits.

The need to consider this class of models is mostly associated with the interpretation of tracer tests during experimental studies of mass transfer (migration)

properties. The regional components of groundwater flows, such as area-distributed infiltration, can be neglected in such cases; however, the role of microdispersion in small-scale processes can be considerable (Chap. 8). Similar problems are associated with forecasting water quality changes in water supply systems in the presence of heterogeneous natural hydrochemical zonality, where changes in the subsurface hydrodynamics (because of a drop in the head at the water intake well contour) cause the input into the aquifer of poorer quality water from either adjacent aquifer or the aeration zone (Chap. 9).

Chapter 8

Models for Tracer Test Analysis and Interpretation

A common approach to characterizing aquifer mass transfer properties is the use of tracer tests. Our focus is mostly on tracer tests that employ a forced flow field induced by injection and/or withdrawal wells. Such tests offer advantages for estimating transport properties in porous and fractured media over natural gradient tracer tests (Hydraulic and tracer testing... , 1996). We also will focus on the analysis of models describing the vertical movement of natural saltwater–freshwater interface in thick groundwater systems. The interpretation of the latter process also results in useful information about solute transport properties of systems featuring natural hydrogeochemical stratification. Those models are next modified to account for density difference between the fluids in contact (see Secs. 12.3 and 14.2).

Analytical models are adapted to the most common experimental configurations. We first consider the situations where a tracer is injected in a flow field with axial-radial symmetry (experiments in divergent and convergent radial flows), and then tracer migration is analyzed in a field represented by more complex flow paths (dipole-type tracer tests). Some models provide closed-form expressions for incorporating technical factors distorting the interpretation of breakthrough curves. The analysis of the theoretical basis for tracer tests suggest that step, square-wave, and pulse inputs are more common for tracer injection. Only nonreactive (conservative) chemical tracers are considered. This chapter provides mostly an overview of analytical solutions for field tracer test planning, analysis, and interpretation, though the intent is not to provide a manual for tracer testing.

The models discussed below are to some extent idealistic. They are not always applicable to real aquifers under field conditions: usually their practical application is seriously restricted by the manifestation of the aquifer's heterogeneity. If the heterogeneity of the tested sites is implicitly “lumped” into the micro-dispersion term of the Fickian-type equation or into mass-exchange coefficients (characterizing solute retention and dispersion in dual porosity media), one may expect the transfer parameters to be strongly affected by the scale. Therefore, it is important to be aware of the limitations associated with extending the short-term local tracer test results to large (regional) forecasting scale. The assessment of the regional macro-parameters is based solely on the monitoring data (field observations of the behavior of the contaminant plumes and environmental tracers).

The relevant scale-dependent phenomena have been the subject of considerable research interest over the past few decades. In a number of researches, it has been shown that tracer tests can play only an auxiliary role, enabling the assessment of parameters responsible for local-scale advection and dispersion. At the same time, tracer tests can be an indispensable technique for understanding contaminant and specific (remediative) substances movement at contaminated sites that are a subject of in situ treatment and remediation. Finally, tracer injections accompanying pumping tests also can be very useful for deciphering the flow properties of groundwater systems.

8.1 Tracer Migration in a Radially Divergent Flow Field

In a divergent flow test, water with a conservative tracer is injected into a recharge well either by a permanent step increase or as a finite pulse input. The tracer concentration is monitored at one or more wells near the recharge well (Fig. 8.1).

8.1.1 Mathematical Background

The mathematical formulation is based on the axial-symmetric presentation of mass transport Eq. 1.25 together with an appropriate set of boundary and initial conditions. The mathematical formulation of models for real processes should incorporate hydrodynamic dispersion and elementary processes of mass transfer related to dual porosity or flow properties stratification of a tested formation. It is only in simplest computations that the consideration is restricted to the advection component of mass flux.

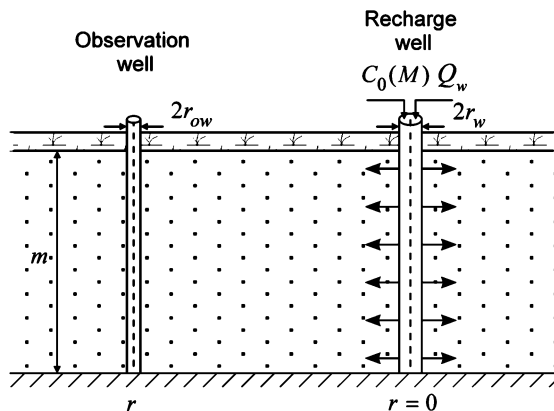


Fig. 8.1 Schematic diagram for the divergent tracer experiment in a confined aquifer

8.1.1.1 Piston-Like Displacement

Let us assume that injection with a constant recharge (volumetric) rate, Q_w , of a tracer solution in a confined aquifer of a constant thickness, m , occurs through a fully penetrating vertical well. Formulas for evaluating the space, r_0 , and time, t_0 , coordinates of fronts (with no account for dispersion) are obtained by directly integrating the advection transport equation:

$$\phi \frac{\partial C}{\partial t} + q_r \frac{\partial C}{\partial r} = 0, \quad q_r = \frac{Q_w}{2\pi r m}, \quad (8.1)$$

which admits a characteristic representation

$$\frac{dr}{dt} = \frac{q}{\phi} = u_r, \quad (8.2)$$

and, upon integration over intervals $[r_w, r_0(t)]$ and $[0, t_0(r)]$, yields:

$$r_0(t) = \sqrt{r_w^2 + \frac{Q_w t}{\pi m \phi}}, \quad t_0(r) = \frac{\pi(r^2 - r_w^2)m\phi}{Q_w}, \quad (8.3)$$

where t is the current time; r is the current coordinate; q_r is the radial specific discharge (radial Darcy velocity); r_w is the recharge well radius; ϕ is the porosity. The same result can be obtained from the obvious balance equation $Q_w t = \pi(r^2 - r_w^2)m\phi$.

A deviation of flow structure from radial (axial-symmetric) one because of aquifer anisotropy in a horizontal plane (characterized by the square root of the anisotropy ratio, $\kappa = \sqrt{k_x/k_y}$, where k_x and k_y are the hydraulic conductivities of the rock formation along appropriate directions) can be accounted for in the model by a correction of time t_0 :

$$t_0 = \frac{\pi m \phi r^2 (\cos^2 \varphi + \kappa^2 \sin^2 \varphi)}{\kappa Q_w}, \quad (8.4)$$

where φ is the angle between the direction to the observation well and the x -axis, which coincides with a principal axis of anisotropy. The disturbing effect of natural groundwater flow can be taken into account in a similar manner (1.80).

8.1.1.2 A Governing Equation and Boundary Conditions

When a flow field is axial-symmetric, convective dispersive flux of a conservative tracer, complicated by mass exchange kinetics between mobile and immobile domains (e.g., due to tracer diffusion from the fracture region into the rock matrix), is described by equation as follows

$$\frac{\partial C}{\partial t} + u_r \frac{\partial C}{\partial r} - \frac{1}{\partial r} \left(D_r r \frac{\partial C}{\partial r} \right) + \frac{W_s}{\phi} = 0; \quad (8.5)$$

here W_s is the transfer rate function corresponding to net solute exchange rate per unit volume of aquifer per unit time [$\text{ML}^{-3}\text{T}^{-1}$]; u_r is the radial flow velocity; D_r is the velocity-dependent coefficient of longitudinal microdispersion,

$$D_r = \delta_L u_r = \frac{\delta_L A}{r}, A = \frac{Q_w}{2\pi m\phi}. \quad (8.5a)$$

As one may see, molecular diffusion, as a component of dispersive flux in the mobile domain, is ignored.

The parameter A [L^2T^{-1}] reflects the rate of flow perturbation and advection in the pore space. In the case of radial water flow in a single fracture, the group $m\phi$ in the expression for parameter A , is replaced by fracture aperture, $2b_f$. An alternative (hydrodynamic) representation of parameter A (Novakowski 1992)

$$A = \frac{\Delta h T}{\ln(r/r_w)m\phi} \quad (8.5b)$$

follows from *Dupuit* formula for a groundwater flow with radial symmetry; here Δh is the difference in hydraulic head between the recharge and observation wells [L]; $T = km$ is confined aquifer transmissivity [L^2T^{-1}]. When a single fracture is tested (Novakowski and Lapcevic 1994),

$$A = \frac{\Delta h \rho g (2b_f)^2}{12\mu \ln(r/r_w)}, \quad (8.5c)$$

where ρ and μ are the density [ML^{-3}] and dynamic viscosity [$\text{ML}^{-1}\text{T}^{-1}$] of tracer solution, g is free fall acceleration [LT^{-2}]. The estimates (8.5b) and (8.5c) can be of use to control the effective thickness of the aquifer or the fracture aperture involved in the formation of groundwater flow in the test site.

Substituting u_r (8.2) and D_r (8.5a) into (8.5) transforms it into

$$\frac{\partial C}{\partial t} + \frac{A}{r} \frac{\partial C}{\partial r} - \frac{\delta_L A}{r} \frac{\partial^2 C}{\partial r^2} + \frac{W_s}{\phi} = 0. \quad (8.6)$$

When the problem is formulated, the tracer input function is often approximated by a simple source term, represented mathematically by a step function of a constant concentration, a square pulse of a concentration input (of duration t_s), or a pulse of a finite tracer mass *directly applied* to the aquifer medium. Thus, for the first scenario we have:

$$C|_{r=r_w} = C_0, \quad (8.7a)$$

where C_0 is solute (tracer) concentration in the solution being injected. The boundary condition at the well ($r = r_w$) in (8.7a) is a first-type condition. In the general

case, a third-type boundary condition (Communar et al. 1986) can be considered on the contour of the recharge well. In the case of a step-wise input, this can be represented in the balance form

$$2\pi m\phi r \left[\frac{A}{r}C - \frac{\delta_L A}{r} \frac{\partial C}{\partial r} \right]_{r=r_w} = Q_w C_0. \quad (8.7b)$$

The left-hand side of this equation accounts for the rate of solute input into the filter interval of the well through its casing, while the right-hand side is for the total weight rate of its discharge into the aquifer due to advection and hydrodynamic dispersion. However, there is no need to complicate the problem in such a manner unless the advection dispersion is to be analyzed in the immediate vicinity of the injection well (within distances comparable with well diameter), where, in the general case, C_0 can be considered a function of time $C_0 = C_0(t)$, in particular, in the case of a heterogeneous initial condition (Veling 2001).

For a short-duration pulse of finite tracer mass, M , into a recharge well, the conditions (8.7a) and (8.5b) correspond to expressions (Chen et al. 2007)

$$C|_{r=r_w} = \frac{M}{Q_w} \delta(t). \quad (8.7c)$$

$$2\pi m\phi r \left[\frac{A}{r}C - \frac{\delta_L A}{r} \frac{\partial C}{\partial r} \right]_{r=r_w} = M \delta(t), \quad (8.7d)$$

where $\delta(t)$ is Dirac delta function.

Additionally, without the loss of generality, one may assume:

$$C|_{t=0} = 0, \quad C|_{r \rightarrow \infty} = 0. \quad (8.7e)$$

Problem formulation for the interpretation of data from the observation wells may require taking into consideration tracer mixing with formation water in wells and the hydraulic resistance of near-well region and hole filters (skin effect) (see Sect. 8.3.1). Under certain experimental conditions, the test results can be distorted by mixing and skin effects related to the source (injection) well (Brouyère et al. 2005).

The search for analytical solutions of the radial problem (8.6)–(8.7) was the focus of many studies. The pioneer works appeared in the 1960s–1970s (Raimondi et al. 1959; Shestakov 1963; Bochever and Oradovskaya 1969; Ogata 1970; Dagan 1971; Gelhar and Collins 1971; Tang and Babu 1979). Efficient numerical solutions for solute transport in a radial flow field were obtained by Hoopes and Harleman (1967a) using the finite difference technique, and Moench and Ogata (1981) with the numerical inversion of the Laplace transform. Those studies were mostly aimed at advective hydrodynamic dispersion in homogeneous rock formations.

Attempts were made later to analyze the radial migration in dual porosity media (Chen 1985; Maloszewski and Zuber 1990; Moench 1995; Reimus et al. 2003).

In some studies solutions of advection–dispersion equations in cylindrical coordinates have been obtained to investigate how scale-dependent dispersion affects solute transport in a radial flow field (Indelman and Dagan 1999; Kocabas and Islam 2000; Chen et al. 2008).

Two approaches can be identified: the first is the searching for exact analytical solutions of the boundary problem in closed analytical form by applying various methods (mostly based on the Laplace transform) to solve problems of mathematical physics; the second approach is to linearize the equations to obtain approximate formulas based on some physical considerations regarding the averaging of the dispersion term (in the case of homogeneous single porosity formations) or the analysis of asymptotic regimes of diffusion in a porous matrix (dual porosity rocks).

8.1.1.3 A General Laplace Transform Solution

The solutions are most often constructed by using Laplace transforms of Eqs. 8.6 and 8.7a:

$$\frac{d^2 \tilde{C}}{d\rho^2} - \frac{d\tilde{C}}{d\rho} = \rho\omega\tilde{C}, \quad (8.8)$$

$$\tilde{C}(\rho = \rho_w) = 1/\bar{p}, \quad \tilde{C}(\rho \rightarrow \infty) = 0; \quad (8.9)$$

$\tilde{C} \equiv \tilde{C}(\bar{p}) = \int_0^\infty \bar{C}(\tau) \exp(-p\tau) d\tau$ is the Laplace transform of dimensionless concentration function ($\bar{C} = C/C_0$); $\bar{p} = p\delta_L^2/A$ is the dimensionless transform parameter; $\rho = r/\delta_L$ (Peclet number, Pe), $\rho_w = r_w/\delta_L$, $\tau = Q_w t / 2\pi m \phi \delta_L^2$ are standardized radial coordinate and time. The representation (8.8) corresponds to the case of a linear dependence of the transform of the source function on concentration (6.42), yielding

$$\omega = \bar{p} + \frac{\delta_L^2}{A} \sigma \tilde{g}(p), \quad (8.10)$$

where $\tilde{g}(p)$ is the Laplace transform of the memory function that has a presentation in the form of Eqs. 6.21a, b for a case of tracer transport in a dual porosity formation.

Substituting (Chen 1985)

$$y = \rho + \frac{1}{4\omega}, \quad C = U \exp\left(-\frac{y}{2}\right) \text{ and } x = \omega^{1/3}y, \quad (8.11)$$

reduces the Eq. 8.8 to

$$\frac{d^2 U}{dx^2} = xU, \quad (8.12)$$

which corresponds to a standard form of *Airy* equation. Its general solution can be written as (Abramowitz and Stegun 1970)

$$U = A\text{Ai}(x) + B\text{Bi}(x) \quad (8.13)$$

or

$$\tilde{C} = Ae^{\rho/2} \text{Ai}(\omega^{1/3}y) + Be^{\rho/2} \text{Bi}(\omega^{1/3}y); \quad (8.14)$$

here A and B are constants of integration; $\text{Ai}(\cdot)$ и $\text{Bi}(\cdot)$ are *Airy* functions of the first and second type determined by *Bessel* functions, $K_m(\cdot)$ and $I_m(\cdot)$, of the order $1/3$ (Abramowitz and Stegun 1970), for example,

$$\text{Ai}(x) = \frac{1}{\pi} \sqrt{\frac{x}{3}} K_{1/3}(\zeta), \text{Bi}(x) = \sqrt{\frac{x}{3}} [I_{-1/3}(\zeta) + I_{1/3}(\zeta)] \left(\zeta = \frac{2}{3} x^{3/2} \right). \quad (8.14a)$$

However, the solution of Eq. 8.8 obtained in terms of *Bessel* functions (Tang and Babu 1979), appears not very good.

The constants A and B in the Eq. 8.14 are determined from the boundary conditions (8.9). The first condition requires $\tilde{C}$ approaching zero with radius r tending to infinity. Since $\text{Bi}(\cdot)$ tends to infinity with indefinitely increasing r , the constant B should be zero. Therefore, the solution (8.14) becomes

$$\tilde{C} = Ae^{\rho/2} \text{Ai}(\omega^{1/3}y). \quad (8.15)$$

The second constant, A , is determined from the boundary condition at the well with $r = r_w$ (8.9):

$$A = e^{-\rho_w/2} \frac{1}{\text{Ai}(\omega^{1/3}y_0)}, \quad y_0 = \rho_w + \frac{1}{4\omega}. \quad (8.15a)$$

Finally, we have:

$$\tilde{C} = \frac{1}{\bar{p}} e^{(\rho - \rho_w)/2} \frac{\text{Ai}(\omega^{1/3}y)}{\text{Ai}(\omega^{1/3}y_0)}. \quad (8.16)$$

The solution (8.16) is the basis for the analysis of migration flows with axial symmetry.

8.1.2 Microdispersion: A Full Analytical Solution

With the sink term for matrix diffusion or other exchange processes within the formation neglected ($W_s = 0$), the expression for parameter ω in Eq. 8.10 ($\omega = \bar{p}$) can be simplified, yielding

$$\tilde{C} = e^{\rho/2 - \rho_w/2} \frac{\text{Ai}(\varphi)}{\bar{p} \text{Ai}(\varphi_0)}, \quad \varphi = \frac{1 + 4\rho\bar{p}}{4\bar{p}^{2/3}}, \quad \varphi_0 = \frac{1 + 4\rho_w\bar{p}}{4\bar{p}^{2/3}}. \quad (8.17)$$

The inverse transform of (8.17) into the original by means of the inversion formula (1.108) yields the solution (Communar et al. 1986; Hsieh 1986):

$$\bar{C} = \bar{C}(\rho, \tau) = 1 - F_0(\rho, \tau), \quad F_0(\rho, \tau) = \exp\left(\frac{\rho - \rho_w}{2}\right) \int_0^\infty \frac{f_0(z)}{\pi z} dz. \quad (8.18)$$

Function $f_0(z)$ can be represented in two forms. According to transformations carried out by Communar with co-workers (1986),

$$f_0(z) = e^{-z\tau} \frac{\text{Ai}(\vartheta_0) \text{Bi}(\vartheta) - \text{Ai}(\vartheta) \text{Bi}(\vartheta_0)}{\text{Ai}^2(\vartheta_0) - \text{Bi}^2(\vartheta_0)}, \quad \vartheta = \frac{1-4\rho z}{4z^{2/3}}, \quad \vartheta_0 = \frac{1-4\rho_w z}{4z^{2/3}}. \quad (8.18a)$$

On the other hand, the solution of the problem obtained by Hsieh (1986) yields

$$f_0(z) = 2e^{-z^2\tau} \frac{\text{Ai}(\vartheta) \text{Bi}(\vartheta_0) - \text{Ai}(\vartheta_0) \text{Bi}(\vartheta)}{\text{Ai}^2(\vartheta_0) + \text{Bi}^2(\vartheta_0)}, \quad \vartheta = \frac{1-4\rho z^2}{4z^{4/3}}, \quad \vartheta_0 = \frac{1-4\rho_w z^2}{4z^{4/3}}. \quad (8.18b)$$

The functions $f_0(z)$ in the two representations are mathematically identical; therefore, numerical integration of (8.18) with $f_0(z)$ defined by (8.18a) or (8.18b), gives practically the same results (Fig. 8.2). Considering that Airy functions widely oscillate within some ranges of the argument, the domain of numerical integration of (8.18) should be divided into several intervals (Communar et al. 1986; Hsieh 1986). An advantageous step is to expand functions into power series (Abramowitz and Stegun 1970; Hsieh 1986).

Plots in Fig. 8.2 can be considered as reference data. They can be used in the analysis of experimental data and estimation of the acceptability of approximate analytical relationships.

The solution (8.18) can serve as the basis for constructing a calculation relationship for a pulse input in a radial flow (8.7c). With this in view, we use formula (1.123), relating the two solutions for basic concentration inputs. We write this formula as

$$\frac{\rho^2}{2} \frac{\partial \bar{C}(\rho, \tau)}{\partial \tau} = \bar{C}_i(\rho, \tau), \quad (8.19)$$

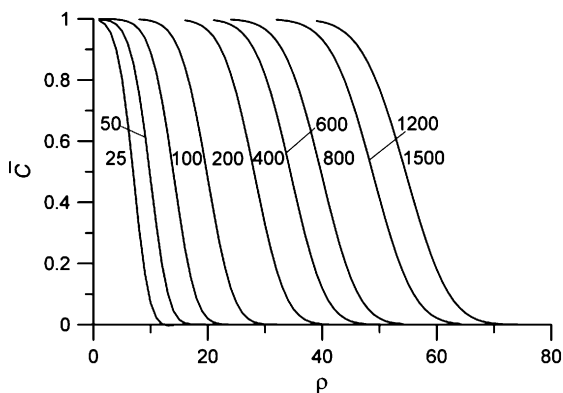


Fig. 8.2 Solutions $\bar{C}(\rho, \tau)$ of radial hydrodynamic dispersion problem obtained by numerical integration of (8.18). Figures at the curves denote the dimensionless time, $\tau = Q_w t / 2\pi m n \delta_L^2$

where

$$\bar{C} \equiv \bar{C}_c = \frac{C}{C_0}, \quad \bar{C}_i = \frac{\pi m \phi (r^2 - r_w^2)}{M} C_i. \quad (8.19a)$$

Differentiating the basic solution (8.18) with respect to τ yields

$$\bar{C}_i = \frac{\rho^2}{2} \exp\left(\frac{\rho - \rho_0}{2}\right) \int_0^\infty \frac{f_0(z)}{\pi} dz, \quad (8.20)$$

or in a dimensional form

$$C_i = \frac{M}{2\pi m \phi \delta_L^2 [1 - (r_w/r)^2]} \exp\left(\frac{\rho - \rho_0}{2}\right) \int_0^\infty \frac{f_0(z)}{\pi} dz. \quad (8.21)$$

The authors of some studies prefer the construction of “reference” solutions based on numerical methods used to invert appropriate Laplace transforms (Chen et al. 2007). In such cases, the model can account for a stricter third-type boundary condition (8.7d).

8.1.3 Approximate Solutions

Approximate solutions of Eq. 8.6 with $W_s = 0$ were obtained under various assumptions, which essentially involve the space or time averaging of the coefficient of longitudinal microdispersion (Raimondi et al. 1959; Shestakov 1963; Hoopes and Harleman 1967a; Roshal 1981; Alexeev et al. 1989; Welty and Gelhar 1994). Such solutions at $(r_w = 0)$ can be represented in the following generalized form:

$$\bar{C} = \frac{1}{2} \operatorname{erfc}\left(\frac{1 - t_r}{\sqrt{2\bar{\sigma}_t^2}}\right), \quad (8.22)$$

where $t_r = Q_w t / \pi m \phi r^2$ is a dimensionless parameter expressed as the ratio of the current duration t of the process of solute migration in an axial-symmetric flow to the characteristic time coordinate of piston-like displacement front, $t_0 = \pi r^2 m \phi / Q_w$ (8.2); $\bar{\sigma}_t^2$ is a dimensionless parameter characterizing the statistical dispersion of concentration points over time and depending, in the general case, on the dimensionless time, t_r , and the Peclet number, $Pe = r/\delta_L$. In our analysis we assume the effect of molecular diffusion negligible compared to the mechanism of hydrodynamic dispersion.

Thus, Raimondi and co-workers (1959) suggested that, at some distance from the injection well, the influence of hydrodynamic dispersion on concentration is small in comparison to the overall dispersive effect that has taken place up to that point (Hoopes and Harleman 1967a; Tang and Babu 1979; Kwok et al. 1995).

Then, in a case of homogeneous aquifer testing ($W_s = 0$), the third term in (8.6) can be ignored, allowing the replacement of the spatial derivative by the temporal derivative: $\partial C / \partial r \approx -(r/A)(\partial C / \partial t)$. By introducing the above approximation and assuming $W_s = 0$, one can rewrite Eq. 8.6 as

$$\frac{\partial C}{\partial t} + \frac{A}{r} \frac{\partial C}{\partial r} - \frac{\delta_L r}{A} \frac{\partial^2 C}{\partial t^2} = 0 \left(A = \frac{Q_w}{2\pi m \phi} \right). \quad (8.23)$$

To reduce the partial differential Eq. 8.23 to an ordinary differential equation, a new variable is introduced:

$$u = (r^2/2 - At)/(4\delta_L r^3/3)^{1/2}, \quad (8.23a)$$

yielding (Tang and Babu 1979)

$$\frac{d^2 C}{du^2} + 2u \frac{dC}{du} = 0. \quad (8.23b)$$

The solution of this equation with $C(r = r_w) = C_0$ can be written as

$$\bar{C} = \frac{C}{C_0} = \frac{\text{erfc}(u)}{\text{erfc}(u_0)}, \quad (8.23c)$$

where $u_0 = u(r = r_w)$. With $r_w \rightarrow 0$, $\text{erfc}(u_0) \rightarrow 2$ and the solution (8.23c) takes the form of (8.22) with

$$\bar{\sigma}_t^2 = \frac{8}{3\text{Pe}}. \quad (8.23d)$$

Shestakov (1963) suggested that dispersion should be regarded only near the concentration front $r = r^* = \sqrt{Q_w t / \pi m \phi}$. Now, introducing $x = \pi r^2$, we obtain the equation

$$\frac{\partial C}{\partial t} + \tilde{u} \frac{\partial C}{\partial x} - \tilde{D} \frac{\partial^2 C}{\partial x^2} = 0, \quad (8.24)$$

similar to advection–dispersion equation with constant coefficients $\tilde{u} = Q/m\phi$ and $\tilde{D} = 4\pi\delta_L r^*/3\phi$ for two-dimensional parallel (linear) mass transport. In this case

$$\bar{\sigma}_t^2 = \frac{8t_r \sqrt{t_r}}{3\text{Pe}}. \quad (8.24a)$$

The formula (8.24a) can be readily obtained by using the generalized solution of Welty and Gelhar (1994) (1.96)/(1.139). Thus, assuming $u(s) = A/r$ ($A = Q_w/2\pi m\phi$) and integrating (1.138a), we obtain

$$\omega(t) = \frac{\bar{r}^3}{3A^2}, \quad t_0(s) = \frac{r^2}{2A}, \quad \bar{r} = \sqrt{2At}. \quad (8.25)$$

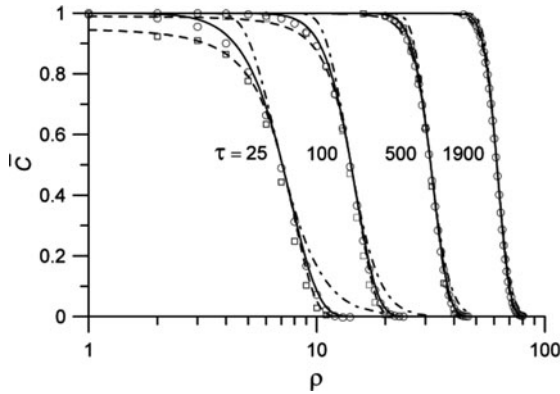


Fig. 8.3 A comparison of different approximate solutions for microdispersion in a divergent radial flow. *Hollow circles* are for the exact solution of (8.18); *dashed line* is the Wely–Gelhar–Shestakov solution (8.22)/(8.24a); *dash-and-dot line* is the solution obtained by Raimondi et al. (8.22)/(8.23d); *full line* is the Roshal solution (8.22)/(8.26); *squares* are for the solution (8.28)

Using these functions to determine the argument ξ (1.139), we come, after simple transformations, to the solution in the form of (8.22)/(8.24a), which coincides with a result obtained earlier (Gelhar and Collins 1971).

Analysis of the solution in Laplace transforms allowed Roshal (1981) to obtain formula (8.22) where

$$\bar{\sigma}_t^2 = \frac{8t_r}{3\text{Pe}}. \quad (8.26)$$

The approximate solutions for axial-symmetric microdispersion considered above are functions of two dimensionless variables, t_r and Pe , allowing them to be compared easily. The errors that arise when approximate solutions are used can be estimated by their correlation with the exact solution of the axial-symmetric problem $\bar{C}(\rho, \tau)$ in the form (8.18), Figs. 8.2 and 8.3, as well as with the earlier numerical solutions expressed in forms of dimensionless breakthrough curves (Hoopes and Harleman 1967a; Sauty 1978, 1980); the dimensionless groups can be related by the equation $t_r = 2\tau/\text{Pe}^2$, with $\text{Pe} \equiv \rho$. It can be seen that with $\text{Pe} > 50$, the relative errors of solutions (8.22)/(8.23d) and (8.22)/(8.24a) do not exceed 10% (for $\bar{C} > 0.2$). In the domain of low Pe values, the solution of Raimondi et al. (1959) overestimates the concentrations at the leading and trailing edges, while the solution of Wely and Gelhar (1994), conversely, underestimates the concentration in these domains. The solution of Roshal (1981) with $\bar{\sigma}_t^2$ in (8.22) determined from (8.26) is more reliable. This solution practically coincides with the exact solution almost throughout the range of Pe values.

It is reasonable to consider the solution of equation

$$\frac{\partial C}{\partial t} + u_r \frac{\partial C}{\partial r} - \frac{D_L}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) = 0, \quad u_r = \frac{Q_w}{2\pi r m \phi}, \quad (8.27)$$

describing the radial transport at constant coefficient of longitudinal dispersion D_L . The Laplace transform of this equation yields an ordinary differential equation of Bessel type (Kamke 1977):

$$\frac{d^2\tilde{C}}{dr^2} + \frac{1}{r}(1-2\nu)\frac{d\tilde{C}}{dr} - \gamma^2\tilde{C} = 0, \gamma^2 = \frac{p}{D_L}, \nu = \frac{Q_w}{4\pi m D_L} \quad (8.27a)$$

(with zero boundary conditions). The solution of Eq. 8.27a with a constant boundary condition $\tilde{C}(r = r_w) = 1/p$ is well known:

$$\tilde{C} = \frac{(r/r_w)K_\nu(\gamma r)}{pK_\nu(\gamma r_w)}, \quad (8.27b)$$

here $K_\nu(z)$ is the modified, ν th-order, second-kind Bessel function.

Using the approximation $K_\nu(z) = \frac{1}{2}\Gamma(\nu)\left(\frac{z}{2}\right)^{-\nu}$, valid at $z \rightarrow 0$ (Abramowitz and Stegun 1970), and assuming $r_w \rightarrow 0$, we can write:

$$\tilde{C} = \frac{(\gamma r)^\nu}{2^{\nu-1}p\Gamma(\nu)}K_\nu(\gamma r), \quad (8.27c)$$

where $\Gamma(\cdot)$ is gamma function. Upon passage from the image to the original, we obtain (Bochever and Oradovskaya 1969):

$$\bar{C} = \frac{1}{\Gamma(\nu)} \int_{1/4Fo}^{\infty} e^{-z} z^{\nu-1} dz, \text{ Fo} = \frac{D_L t}{r^2}. \quad (8.28)$$

Numerical analysis shows that when $Pe > 20 - 30$ the solution (8.28) also adequately describes the radial dispersion with variable coefficient D_L (Fig. 8.3), if, when determining the *Fourier* number, Fo (8.28), which combines the space and time coordinates, we take

$$D_L = \delta_L u_r = \delta_L \frac{Q_w}{2\pi r m \phi}.$$

Now $Fo = t_r/2$ $Pe = \tau/Pe^3$, $\tau = Q_w t/2\pi m \phi \delta_L^2$, $\nu = Pe/2$, $Pe \equiv \rho = r/\delta_L$.

The concentration functions corresponding to a pulse input of the tracer into the injection well can also be described by using statistical characteristics t_r and σ_i^2 : the solution takes the form similar to the expression for the normal probability distribution density (Alexeev et al. 1989), i.e.

$$\bar{C}_i = \frac{1}{\sqrt{2\pi\sigma_i^2}} \exp(-\xi^2), \xi^2 = \frac{(1-t_r)^2}{2\sigma_i^2}, \quad (8.29)$$

where the relative and absolute concentrations are related by the expression (8.19a). The situation with a square pulse of concentration input of tracer is described by the superposition (8.22) of solutions (1.125).

8.1.4 Tracer Tests in Fractured-Porous Aquifers

In an ideal case, an appropriate model for interpretation of a tracer test in a dual porosity aquifer should consider both Fickian matrix diffusion and radially divergent microdispersion. Considering the relatively short duration of field experiments, the most asked-for among the models describing tracer transfer between fracture and porous matrix domain is the model of unlimited matrix diffusion (Sect. 6.1). The solution of the problem in Laplace transforms is expressed by (8.16) in which

$$\omega = \bar{p} + \frac{1}{\text{Pe}} \sqrt{2B_m t_0 \bar{p}}, \quad (8.30)$$

where $B_m = \sigma^2 \lambda_m$ for a uniformly fractured dual porosity aquifer characterized by lumped transfer coefficient λ_m (6.11), $B_m = D_m \phi_m^2 / b_f^2$ for a single fracture with aperture $2b_f$ surrounded by porous matrix (see Sect. 6.1.3).

The inversion of (8.16) with ω determined from (8.30) into the real-time domain involves considerable mathematical complications. Therefore, numerical methods are most often used to obtain rigorous solutions for such inversion (Moench 1995; Reimus et al. 2003; see also Sect. 1.3.3). Approximate solutions are obtained with some physical assumptions, which will be discussed below.

8.1.4.1 A Solution for Advective (Piston-Like) Displacement of Groundwater by the Injected Tracer

The solution of the radial problem (8.16) in Laplace transforms can be simplified considerably if the dispersion component of mass transfer is neglected by assuming $\delta_L = 0$. After some algebraic transformations and the scaling of the complex variable p relative to the characteristic time of the process t_0 , we come to an expression for the piston-like displacement of the initial solution by the tracer solution

$$\tilde{C} = \frac{1}{\bar{p}} \exp \left[- \left(\bar{p} + \sqrt{B_m t_0 \bar{p}} \right) \right], \quad \bar{p} = t_0 p. \quad (8.31)$$

Using the tables for inverse transform (Bateman and Erdelyi 1954), we obtain

$$\bar{C} = \text{erfc} \left(\frac{\sqrt{B_m t_0}}{2\sqrt{t_r - 1}} \right), \quad t_r = \frac{t}{t_0} = \frac{Q_w t}{\pi m \phi (r^2 - r_w^2)} \geq 1. \quad (8.32)$$

The solution (8.32), associated with the *Lauverier* formula for the linear problem (6.24), also can be written as

$$\bar{C} = \text{erfc}(\xi), \quad (8.33)$$

where

$$\xi = \frac{\sqrt{\bar{\lambda}}}{2} \sqrt{\frac{t_0}{t - t_0}}, \quad \bar{\lambda} = B_m t_0, \quad t \geq t_0 = \frac{\pi(r^2 - r_w^2)m\phi}{Q_w}. \quad (8.33a)$$

Another solution of Eq. 8.6 with the same assumption was obtained by the method of moments in the generalized integral form (Mironenko and Rumynin 1986)

$$\bar{v}_1 = \int_0^\infty \bar{C} r dr = \frac{Q_w}{2\pi B_m m \phi} W(B_m t), \quad (8.34)$$

where the generalized parameter B_m characterizes mass exchange and the storage characteristic of blocks and fractures (see above);

$$W(B_m t) = 2\sqrt{\frac{B_m t}{\pi}} + e^{B_m t} \operatorname{erfc} \sqrt{B_m t} - 1. \quad (8.35)$$

Analysis of the solution (8.34) allows some useful balance relationships to be established. Thus, considering that the characteristic $\bar{v}_1$ is directly related with the amount of matter in the system of fractures $P_m = 2\pi m \phi C_0 \bar{v}_1$, one can readily estimate its share in the total volume of dissolved solute $P_0 = Q_w C_0 t$, pumped into the aquifer through the well by time t ,

$$\frac{P_m}{P_0} = \frac{W(B_m t)}{B_m t}. \quad (8.36)$$

Note that when

$$B_m t < 0.1, \quad (8.37)$$

$W(B_m t) \approx B_m t$, i.e., as it follows from formula (8.36), almost all the solute is contained in fractures. Therefore, when (8.37) is true, microdispersion model for single porosity aquifer can be applied (Sects. 8.1.2 and 8.1.3). With the condition

$$B_m t > 5 \quad (8.38)$$

$W(B_m t) \approx \sqrt{B_m t}$, whence it follows that $P_m/P_0 \approx 1/\sqrt{B_m t}$, i.e., the major portion of the solute injected into the bed is spent in this case for the saturation of the porous matrix, hence the storage capacity of fractures almost does not control the process (except for the leading zone of the concentration wave with $\bar{C} < 0.15 - 0.2$).

Under quasi-stationary regime of mass exchange between fractures and rock blocks, which is described by a *first-order mass transfer model*, one can use a generalized solution of the problem (6.31), in which the time coordinate of the piston-like displacement front for radial two-dimensional flow t_0 is determined by the second formula in (8.3).

8.1.4.2 The Effect of Hydrodynamic Dispersion

An assumption of piston-like tracer displacement in fracture domain can be found to be too rough for small-scale tracer experiments, when a field of higher and

abruptly varying flow velocities forms around the injection well. The effect of microdispersion in fractures can be efficiently taken into account in the integral representation of solution in the form of (6.52). The dimensionless form of solution (6.52) for tracer dispersion in dual porosity reservoir with radial flow geometry is as follows:

$$\bar{C} = \int_0^{t_r} \frac{\partial \bar{C}'}{\partial \theta} \operatorname{erfc} \left(\frac{\sqrt{\bar{\lambda}}}{2} \frac{\theta}{\sqrt{t_r - \theta}} \right) d\theta, \quad \bar{\lambda} = B_m t_0 \quad (8.39)$$

($r_w \ll r$), and the derivative $\partial \bar{C}'(\theta)/\partial \theta$ under the integral is determined from the solution of appropriate hydrodynamic dispersion problem in an equivalent homogeneous (single porosity) formation (see Sects. 8.1.2 and 8.1.3).

Thus, differentiating (8.22) with $\bar{\sigma}_t^2$ determined by (8.26) yields

$$\frac{\partial \bar{C}'}{\partial \theta} = \frac{\sqrt{3}}{8\pi\sqrt{\theta/\operatorname{Pe}}} \left(\frac{1+\theta}{\theta} \right) \exp \left(-\frac{3(1-\theta)^2 \operatorname{Pe}}{16\theta} \right), \quad \operatorname{Pe} = \frac{r}{\delta_L}. \quad (8.40)$$

Variants of calculation based on solution (8.39) correspond to various values of complex parameters $\bar{\lambda}$ and Pe (Fig. 8.4). The accepted interval of variations in $\bar{\lambda}$ embraces media with relatively high and low matrix diffusion (transfer) characteristics. Analysis of the obtained results (Fig. 8.4) shows that the contributions of different migration mechanisms to the general process controlling breakthrough curve behavior are determined by ratios between solute transfer parameters λ_m , δ_L , and ϕ and depend, other conditions being the same, on the distance, r , and the recharge rate, Q_w .

The subordinate role of hydrodynamic dispersion in fractured media with high matrix diffusion characteristics and the weakness of kinetic exchange processes in media with low matrix diffusion characteristics justify the application, as approximations, of simpler asymptotic solutions (8.33) and (8.22). At the same time, the significance of matrix diffusion kinetics and longitudinal dispersion can be comparable in intermediate cases.

As applied to tracer experiments, the joint effect of kinetics of mass transfer and microdispersion dramatically increases the uncertainty in the interpretation of experimental results with the use of simplified calculation schemes and hence, the errors in evaluating mass transfer parameters. Thus, when mass exchange parameters are low, the underestimation of the role of hydrodynamic dispersion in fractures can lead to relative errors in concentration estimates by (8.33) reaching tens or, when $\bar{C}$ is small (less than 0.15–0.2), even hundreds percent. Accordingly, errors in estimates of λ_m also can reach several hundred percent. The errors will be somewhat less for fracture density ϕ , but the behavior of the error function is very complex: it can increase in the domain of not only small, but also large concentrations as well.

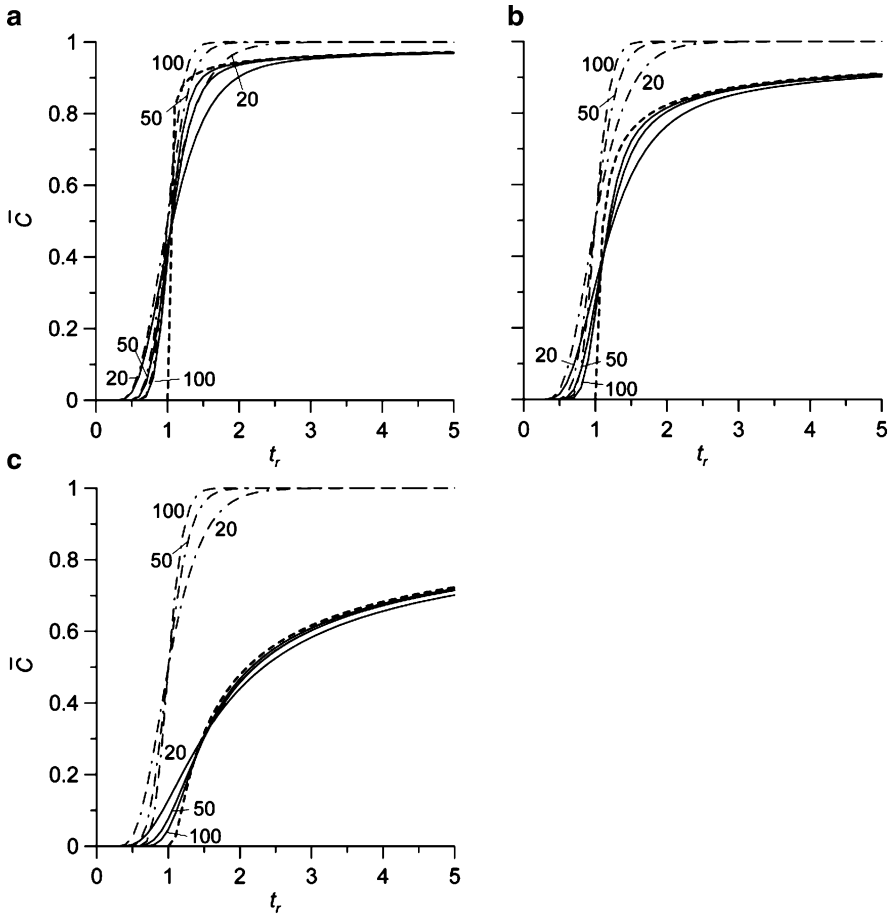
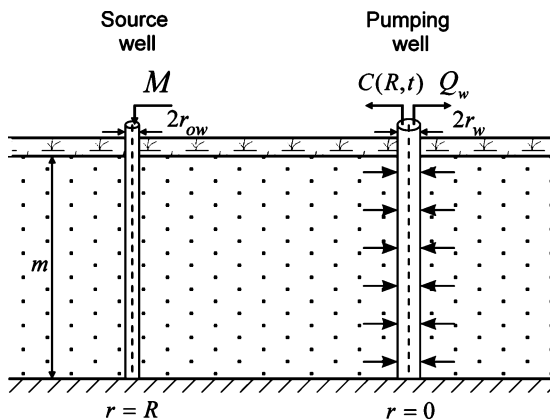


Fig. 8.4 Data for the analysis of the joint effect of hydrodynamic dispersion and matrix diffusion kinetics within the fractured porous reservoir on the breakthrough curves. The values of complex mass exchange parameter, $\bar{\lambda}$: (a) $\bar{\lambda} = 0.01$, (b) $\bar{\lambda} = 0.1$, (c) $\bar{\lambda} = 1.0$. Figures at curves are Peclet number, Pe. Full lines are for calculations by (8.39), dashed lines are for (8.39); and dash-and-dot lines are for (8.22)/(8.26)

8.2 Tracer Migration in a Radially Convergent Flow Field

The considered experimental scheme is associated with a tracer injection into a convergent flow through a source well located at some radial distance, R , away from the pumping well (Fig. 8.5). The arrival of the tracer at the pumping well is monitored by sampling the pumped water. Notwithstanding the well-known drawbacks (Mironenko and Rumynin 1986), such approach has some advantages over injection tests, including (a) engineering simplicity; (b) the possibility to combine the

Fig. 8.5 Schematic diagram for the convergent tracer experiment



tests with the main hydrogeological studies: aquifer hydraulic testing with multiple boreholes; (c) the amount of tracer recovered can be readily computed, allowing one to effectively control the reliability of the use of a model for the interpretation of test results. There are various modifications of the tests, differing, primarily, in the scenarios for a tracer input in the radially convergent flow. For example, the tracer may be introduced as a pulse of a finite tracer mass (basic scenario), a constant-concentration injection, or a squared-pulse concentration input. The tracer solution pumped out of the central well can also be reinjected into the tracer injection well (provided that $Q_{wi} \ll Q_w$, where Q_w and Q_{wi} are the pumping-out and injection rates).

Tracer tests in a convergent flow are among the experimental tools most frequently used to estimate effective transport parameters related to equivalent homogeneous aquifers, primarily, the apparent porosity and longitudinal dispersivity coefficient. In exceptional cases, convergent flow tracer tests having been carried out in fractured or stratified aquifers provide possible estimates of porous matrix transfer coefficients or variations in profile hydraulic conductivity.

8.2.1 *On the Application of Approximated Models with Linear Geometry and the Assessment of Distorting Factors*

Approximate estimates, though quite sufficient for practice, are often derived by transforming linear one-dimensional models (Kreft et al. 1974; Zuber 1974; Maloszewski and Zuber 1990), considered earlier for basic pulse Dirac function, e.g., (1.120) (for homogeneous single porosity rock formations) and (6.27) (for fractured-porous/dual porosity rocks). In such transformations, the dimensionless concentration, $\bar{C}_i$, corresponds to the real concentration, C_i , divided by the initial concentration in the pulse, C_0 . In its turn, the concentration C_0 is defined as the ratio of the injected tracer mass, M , to the volume of a cylinder with height m

(*confined aquifer*) and radius R , equal to the distance between the pumping-out and tracer-injection wells, i.e.,

$$\bar{C}_i = \frac{C_i}{C_0}, C_0 = \frac{M}{\pi(R^2 - r_w^2)m\phi}. \quad (8.41)$$

The pulse approximation of the input concentration function is not always good, as theoretical analysis (Welty and Gelhar 1994; Zlotnik and Logan 1996; Brouyère et al. 2005) and field measurements (Becker and Charbeneau 2000) show the concentration in the injection well to decrease exponentially because of the gradual dilution of solute in the well by background water entering it (see Sect. 8.3.2).

Next, the dimensionless groups $\bar{t}$ and Pe in linear approximate solutions for radial migration are defined as

$$\bar{t} \equiv t_R = \frac{t}{t_0}, t_0 = \frac{\pi m \phi (R^2 - r_w^2)}{Q_w} \text{ and } Pe = \frac{R}{\delta_L}, \quad (8.42)$$

where R is the distance between wells, r_w is the radius of pumping-out well.

Water withdrawal from an *unconfined aquifer*, being tested with the use of tracer injections (Kreft et al. 1974; Zuber 1974), results in the formation of a cone of depression, such that its water-bearing thickness, m , is not constant: $m = h(r)$. Therefore, to correct calculation schemes involving the use of characteristic time t_0 , we write the kinematic condition of particle motion in the field of the pumping-out well as

$$\frac{dr}{dt} = -\frac{Q_w}{2\pi h(r)\phi r}, \quad (8.43a)$$

where the current flow thickness can be calculated from the Dupuit formula

$$h(r) = \sqrt{h_w^2 + \frac{Q_w}{\pi k} \ln\left(\frac{r}{r_w}\right)}, \quad (8.43b)$$

h_w is the water-bearing thickness of the aquifer at the well contour; k is rock hydraulic conductivity.

Substituting (8.43b) into (8.43a) and integrating yields the following formula for the characteristic time

$$t_0 = -\frac{2\pi\phi}{Q} \int_R^{r_w} r \sqrt{h_w^2 + \frac{Q_w}{\pi k} \ln\left(\frac{r}{r_w}\right)} dr, \quad (8.43c)$$

where one can readily see that t_0 is nothing less than the ratio V/Q_w , where V is the volume of water contained within the aquifer with a free water surface between sections R and r_w .

Integrating (8.43c) by parts yields the dependence (Chapuis and Chesnaux 2006)

$$t_0 = \phi \sqrt{\frac{2\pi}{kQ_w}} [R^2 g(R) - r_w^2 g(r_w)] + \frac{r_w^2 \sqrt{\pi}}{2C} [\operatorname{erfi}(g(R)) - \operatorname{erfi}(g(r_w))], \quad (8.44)$$

where $\operatorname{erfi}(z)$ is the implicit error function defined as $\operatorname{erfi}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{y^2} dy$, $g(r) = \sqrt{\ln(Cr^2/r_w^2)}$ ($r = R, r_w$), $\ln C = 2\pi k h_w^2 / Q_w$. Numerical estimates (Chapuis and Chesnaux 2006) show that when $h_w/m \geq 0.5$, the errors in estimating the time t_0 by (8.42), where m is the initial flow thickness, do not exceed a few percent.

The input of solute into the aquifer under *unsteady-state flow regime* (at the moment when pumping starts) also causes some difference between the actual time t_0 and the values obtained from (8.42) because of the involvement of elastic or gravitation water reserves in the aquifer (Mironenko and Rumynin 1998a):

$$t_0 = \frac{\pi(R^2 - r_w^2)m\phi}{(1 - \beta)Q_w}, \quad (8.45)$$

where $\beta = e^{-\sqrt{\alpha}}$, $\alpha = \pi a^* m \phi / Q_w$; a^* is the hydraulic diffusivity [$L^2 T^{-1}$]. As one can readily see, this effect can be undoubtedly neglected since commonly $\beta \ll 1$.

The *natural groundwater flow*, which deforms the radial flow structure, has the strongest effect on the solute migration time (see Sect. 1.2.2.3). Only when the criterion

$$\frac{q_0 m R}{Q_w} < 0.025 \quad (8.46)$$

is true (q_0 is the specific discharge of the natural gradient flow), this effect can be neglected, assuming that errors in migration time estimate t_0 by the formula for axial-symmetric migration will not exceed 10% (in the least favorable case when the injection well is located downstream or upstream of the pumping-out well).

The neglect of the radial flow configuration in one-dimensional models used to interpret test data can cause serious errors in dispersion parameter estimates. The solutions of problems by using mathematical (numerical) models (Wang and Crampon 1995) show that the errors due to the radial symmetry of groundwater flow are largest when Peclet numbers are small and can have different signs depending on the individual one-dimensional solution. Thus, when the concentration function is calculated by using the solution (1.120) for an impulse in a semirestricted medium, the concentration in the domain $t > t(C = C_{\max})$ will be appreciably underestimated, i.e., the role of “tail” effects will not be paid adequate attention. However, the leading front at the migration stages $t < t(C = C_{\max})$ will be described with a sufficient accuracy (when $Pe > 3$). Conversely, the solution for a pulse in an unlimited one-dimensional space (Leij and Torido 1995) yields an appreciable lag in the positions of points on the leading front and more pronounced effects of matter dispersion at $t > t(C = C_{\max})$ relative to the numerical solution.

8.2.2 Microdispersion of Tracer in a Homogeneous Single Porosity Aquifer

8.2.2.1 Laplace Transform Solutions

The differential equation of mass transport in cylindrical coordinates is similar to Eq. 8.5; however, the radial velocity u_r in it has the opposite sign (since the flow is directed against the direction of the r -axis):

$$u_r = -A/r, A = Q_w/2\pi m\phi. \quad (8.47)$$

The solutions of the radial problem differ in the character of specifying boundary conditions. In papers by Moench (1989, 1991, 1995) and Novakowski with co-workers (1992), the process is considered in a spatially *limited* domain ($r_w \leq r < R$): the contour $r = R$, where the injection well is situated, corresponds to a third-type boundary condition (the tracer dilution in the well and its skin-effect are taken into account in some variants, see below); therefore, in a dimensionless form, the governing system of equations for a concentration pulse (in the form of Dirac delta function) in a bounded domain becomes

$$\frac{1}{\text{Pe}} \frac{1}{\bar{r}} \frac{\partial^2 \bar{C}}{\partial \bar{r}^2} + \frac{1}{\bar{r}} \frac{\partial \bar{C}}{\partial \bar{r}} = \frac{2}{1 - \bar{r}_w^2} \frac{\partial \bar{C}}{\partial t_R}, \quad (8.48a)$$

$$\left| \frac{1}{\text{Pe}} \frac{\partial \bar{C}}{\partial \bar{r}} - \bar{C} \right|_{\bar{r}=1} = \delta(\tau), \tau > 0, \left. \frac{\partial \bar{C}}{\partial \bar{r}} \right|_{\bar{r}=\bar{r}_w} = 0, \bar{C}(\bar{r}, 0) = 0, \quad (8.48b)$$

where

$$\bar{r} = \frac{r}{R}, \bar{r}_w = \frac{r_w}{R}, \text{Pe} = \frac{R}{\delta_L}, t_R = \frac{t}{t_0} = \frac{Q_w t}{\pi m \phi (R^2 - r_w^2)}, \bar{C} = \frac{M}{\pi m \phi (R^2 - r_w^2)}.$$

The solution of Eq. 8.48a under conditions (8.48b) has the following generalized representation in Laplace transforms (Moench 1989, 1991; Chen et al. 2002):

$$\tilde{C}(\bar{p}) = \exp \left[\frac{1}{2} (\text{Pe} - \text{Pe}_w) \right] \Omega(\bar{p}), \quad (8.49)$$

where $\Omega(\bar{p})$ is a function depending on a combination of Airy functions (8.14a):

$$\Omega(\bar{p}) = \Omega(\omega^{1/3} y_R, \omega^{1/3} y_0), \quad (8.49a)$$

$$y_R = \text{Pe} + \frac{1}{4\omega}, y_0 = \text{Pe}_w + \frac{1}{4\omega}, \omega = \frac{2\bar{p}}{\text{Pe}^2 - \text{Pe}_w^2}, \text{Pe}_w = \frac{r_w}{\delta_L}. \quad (8.49b)$$

A solution with a structure similar to (8.16) for the migration process under study was also obtained by solving the inverse *Fokker-Planck* equation (Becker and Charbeneau 2000). It can be represented in the following dimensionless form:

$$\tilde{C}(\bar{p}) = \psi \exp\left[\frac{1}{2}(\text{Pe} - \text{Pe}_w)\right] \Omega(\bar{p}), \quad (8.50)$$

$$\Omega(\bar{p}) = \frac{\text{Ai}(\omega^{1/3} y_R)}{\text{Ai}(\omega^{1/3} y_0)}, \quad (8.50a)$$

$\text{Ai}(\cdot)$ is Airy function, y_R and y_0 are determined from the first two expressions in (8.49b), and $\omega = 2\bar{p}/\text{Pe}^2$.

The solution (8.50) is written in the form involving a “transfer function” (the second and third factors), such that coefficient ψ reflects the form of the input concentration signal. For δ -function, $\psi = 1$; assigning $\psi = A$ (see expressions (1.124)) allows us to incorporate in the images other conditions in the entry point of solute into the formation. Unlike Moench’s solution (8.49), the solution (8.50) was obtained under the assumption that the input boundary is open, i.e., the process is considered in a *semibounded* domain ($0 \leq r < \infty$).

Consider one more mathematical formulation of a boundary problem for a convergent axial-symmetric flow under the assumption that the input boundary $0 \leq r < \infty$ is open (Chen et al. 1996):

$$\frac{1}{\text{Pe}} \frac{1}{\bar{r}} \frac{\partial^2 \bar{C}}{\partial \bar{r}^2} + \frac{1}{\bar{r}} \frac{\partial \bar{C}}{\partial \bar{r}} + \delta(1 - \bar{r}) \delta(t_R) = \frac{2 \partial \bar{C}}{\partial t_R}. \quad (8.51)$$

The solution of Eq. 8.51 in Laplace transforms (Chen et al. 1996), obtained under the boundary conditions

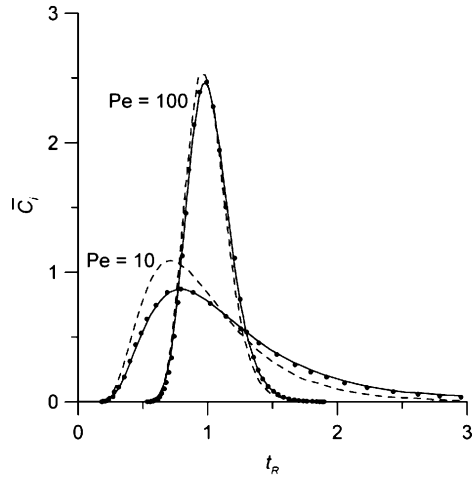
$$\bar{C}(\bar{r}, 0) = 0, \quad \left. \frac{\partial \bar{C}}{\partial \bar{r}} \right|_{\bar{r}=\bar{r}_w} = 0, \quad \bar{C}(\bar{r} \rightarrow \infty, t_R) = 0, \quad (8.51a)$$

allows the dispersion displacement of solute upstream of the injection well to be taken into account. The solution of the problem (8.51)–(8.51a) also includes a combination of Airy functions.

Various numerical algorithms (see Sect. 1.3.3) are available for inverse transformation of solutions in Laplace transforms (8.49) and (8.50) into the real domain with a high accuracy. The use of these algorithms enabled the construction of typical curves $\bar{C}(\text{Pe}, t_R)$, applicable for processing tracer experiments (Moench 1989, 1991, 1995; Chen et al. 1996; Becker and Charbeneau 2000).

Analysis of plots of $\bar{C}(\text{Pe}, t_R)$ shows practically complete coincidence of solutions at $\text{Pe} \geq 100$. In the domain of small characteristic Peclet numbers ($\text{Pe} < 100$), Moench’s solution yields higher concentration peaks and less pronounced “tail” effects as compared with the model (8.50) and the solution of Chen with coauthors (Chen et al. 1996). Moreover, the last two solutions practically coincide, as shown in Fig. 8.6. The wider scatter of the points in the corresponding breakthrough curves is attributed to the physical dispersion of tracer near the injection well in the domain $r \geq R$.

Fig. 8.6 Graphical comparison of the results of numerical inversion of various solutions in Laplace transforms for the problem of a pulse tracer injection into an axial-symmetric convergent flow. *Dashes* are Moench's solution (1989), *dots* are Becker and Charbeneau's solution (2000), *full line* is Chen et al. solution (1996)



8.2.2.2 Approximate Solution of Welty and Gelhar (1994)

The construction of this solution is based on the generalized solution (1.140), describing tracer dispersion in groundwater flow with variable velocity. Suppose that the pumping-out well is located in the point $r = 0$, the position of the injection well is the point $r = R$ ($s = 0$), the radial pore velocity is $u(s) = -A/r$. Now the integral functions $\omega(t)$ and $t_0(s)$ (1.138a) are defined as (Welty and Gelhar 1994)

$$\omega(t) = \int_0^{\bar{s}} \frac{ds}{[u(s)]^2} = \int_{\bar{r}}^R \frac{r^2 dr}{A^2} = \frac{R^3 - \bar{r}^3}{3A^2}, \quad (8.52)$$

$$t_0(s) = \int_0^s \frac{ds}{u(s)} = - \int_R^r \frac{r dr}{A} = \frac{R^2 - r^2}{2A}. \quad (8.52a)$$

The mean time of tracer migration, t , from point $\bar{s} = \bar{r}$ can be found from the condition $r = \bar{r}$ in the equality (8.52a), such that $t_0(\bar{s})$ is

$$t = (R^2 - \bar{r}^2)/2A. \quad (8.52b)$$

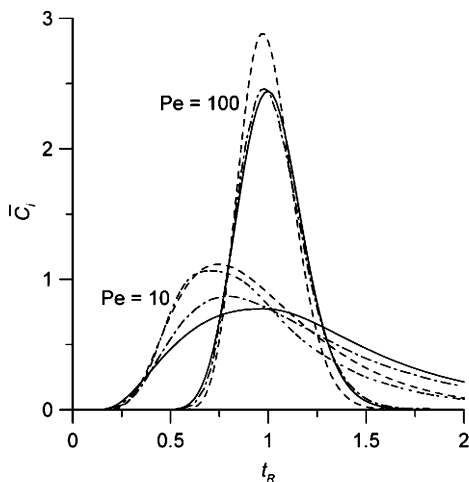
By using (8.52a) and (8.52b) in the second equality (1.138a), we obtain

$$\eta = (r^2 - \bar{r}^2)/2A. \quad (8.52c)$$

In the case of a convergent radial flow, we should set in (1.140)

$$M/A_0 = M/2\pi mR. \quad (8.52d)$$

Fig. 8.7 Comparison of different solutions of the problem of axial-symmetric migration of a tracer in a converging groundwater flow. Full and dashed lines are approximate analytical solutions obtained by [Welty and Gelhar \(1994\)](#) and (1.120), dash-and-dot lines are solutions of [Chen et al. \(1996\)](#), dash-double dot lines are Moench's solutions ([1989, 1991](#)): for $Pe = 100$, it practically coincides with the full line



Substituting (8.52d) (8.52), (8.52a) and (8.52b) into (1.140) with $r = |R^2 - 2At|^{1/2}$ (see (8.52b)) and $u(s_0) = A/R$ yields the general solution of the problem. The resulting solution for the point where concentration is recorded ($r = 0$) becomes

$$\bar{C}_i = \frac{1}{\sqrt{16\pi\psi(t_R)/3Pe}} \exp\left[-\frac{(1-t_R)^2}{16\psi(t_R)/3Pe}\right], \quad (8.52e)$$

$$\bar{C}_i = \frac{\pi m \phi R^2}{M} C_i, \quad \psi(t_R) = 1 - (1-t_R)|1-t_R|^{1/2}, \quad (8.52f)$$

where t_R and Pe are determined by (8.42).

As can be seen from the plot (Fig. 8.7), when Peclet number is large (in this case, $Pe=100$), the solution (8.52e) almost completely coincides with the solutions using Laplace transforms obtained by [Moench \(1989, 1991\)](#) and [Chen et al. \(1996\)](#). When Peclet number is small, the approximate solution (8.52e) is closer to the latter solution, and the transformed one-dimensional linear solution (1.120) shows better agreement with [Moench's \(1989, 1991\)](#) numerical results. Note also that at low Pe , dispersion shifts peaks on curves into the domain left of the characteristic value $\tau = 1$, corresponding to the piston-like displacement front. This means that taking the point $C_{\max}(\tau_{\max})$ on the breakthrough curve as a time-coordinate of the concentration front (8.3) will result in underestimation of the calculated porosity value.

8.2.3 Tracer Transport in a Fractured-Porous Aquifer

Laplace transform of the radial mass transfer equation (8.5) for converging groundwater flow (8.47) for asymptotic (6.21a) (a model of unlimited matrix diffusion) yields an ordinary differential equation

$$\frac{1}{\text{Pe}} \frac{d^2 \tilde{C}}{d\tilde{r}^2} + \frac{d\tilde{C}}{d\tilde{r}} = \frac{2\tilde{r}\tilde{C}}{1 - \tilde{r}_w^2} \bar{\chi}, \quad \bar{\chi} = \bar{p} + \sqrt{B_m t_0 \bar{p}}, \quad \bar{p} = p t_0, \quad t_0 = \frac{\pi m \phi (R^2 - r_w^2)}{Q_w} \quad (8.53)$$

The boundary conditions for this equation have the form

$$\left| \frac{1}{\text{Pe}} \frac{\partial \tilde{C}}{\partial \tilde{r}} - \tilde{C} \right|_{\tilde{r}=1} = 1, \quad \left| \frac{\partial \tilde{C}}{\partial \tilde{r}} \right|_{\tilde{r}=\tilde{r}_w} = 0. \quad (8.53a)$$

The general solution of the problem (8.53)–(8.53a) is given by the formula (8.50) (Becker and Charbeneau 2000; Reimus et al. 2003; Zhou et al. 2007) with

$$\omega = \frac{2}{(\text{Pe}^2 - \text{Pe}_w^2)} \left(\bar{p} + \sqrt{B_m t_0 \bar{p}} \right). \quad (8.53b)$$

The inverse Laplace transform of (8.50) with (8.53b) is commonly made by numerical methods (Moench 1995).

The results of tracer experiments can also be processed by using linear approximate solutions, involving the change of variables according to (8.41) and (8.42). In this context, it can be of use to apply Maloszewski and Zuber's solution (1990), transformed into

$$\bar{C}_i(t_R) = \frac{C_i Q_w t_0}{M} = \frac{\sqrt{\bar{\lambda} \text{Pe}}}{4\pi} \int_0^{t_R} \exp \left[-\frac{(1-\tau)^2}{4\tau} \text{Pe} - \frac{\bar{\lambda} \tau^2}{4(t_R - \tau)} \right] \frac{d\tau}{\sqrt{\tau(t_R - \tau)^3}}. \quad (8.54)$$

where the dimensionless time, t_R , and Peclet number, Pe , are defined by (8.42).

If dispersion can be neglected, the solution for a pulse input can be obtained by inverting the transformation (1.121). This involves differentiating the solution of the radial problem in the form of (8.33), resulting in the following dimensionless formula:

$$\bar{C}_i(t_R) = \frac{C_i Q_w t_0}{M} = \frac{\sqrt{\bar{\lambda}}}{\sqrt{4\pi(t_R - 1)^3}} \exp \left[-\frac{\bar{\lambda}}{4(t_R - 1)} \right], \quad \bar{\lambda} = B_m t_0. \quad (8.55)$$

The reliability of interpretation of experiments based on this solution is lower because of the strong manifestation of hydrodynamic dispersion in fractures in the case of a pulse input; this effect is especially significant in the estimates of the mass exchange parameter. Again, the reliability can be low for estimates of active fracture factor ϕ based on a balance relationship for the time of peak concentration output, $t_{\max}$, when it is assumed that $t_{\max} = \pi m \phi r^2 / Q$. It can be shown that the real position of concentration peak on the time plot is

$$t_{\max} = t_0 \left(1 + \frac{\bar{\lambda}}{6} \right), \quad (8.55a)$$

i.e., the mass exchange between fractures and blocks increases the time of $t_{\max}$ attainment, as can be seen from the analysis of plots in Fig. 8.8.

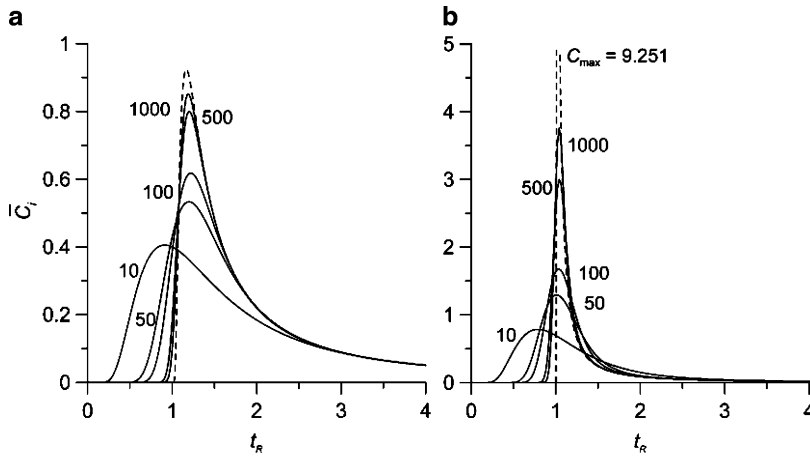


Fig. 8.8 The effect of matrix porosity and microdispersion on the results of a divergent tracer experiment. (a) $\bar{\lambda} = 1.0$, (b) $\bar{\lambda} = 0.1$. Full lines are for solution (8.54), figures on the plot are Pe values; dashed lines are for solution (8.55), Pe=0

8.3 The Time Lag for Breakthrough Curves and Tracer Dilution in a Source Well

8.3.1 The Time Lag for Breakthrough Curves Detected in an Observation Well

The lower throughput capacity of a mud fill zone around an observation well and the dilution of tracer in well-casing, initially filled with formation water, result in that tracer concentration in the aquifer, C , (at the external wall of the well) differs from the concentration in the well, C_w . The duration of the time during which this difference persists can be comparable with the duration of the test itself. During this period, the concentration in the well, C_w , is smaller than C . Consequently, using a real observation well with a finite mixing volume inside and altered permeability of the well wall as a result of drilling (skin effect), one may expect a time delay in the detection of breakthrough curve in comparison with analytical prediction for ideal monitoring system presented by “zero-volume well” (Mironenko and Rumynin 1979, 1986; Novakowski 1992; Welty and Gelhar 1994; Reimus et al. 2003).

To obtain the particular solution for concentration in an observation well, C_w , the effects of mixing in well and skin can be included in a model by specifying the appropriate boundary condition at the test interval. When diffusion exchange at the interface of aquifer and well wall is ignored, an equation for tracer mass balance in a watered well interval of a thickness m can be written in the following one-dimensional form:

$$\pi r_{ow}^2 m \frac{\partial C_w}{\partial t} dt = 2r_{ow} \xi m q_r (C - C_w) dt, \quad (8.56)$$

where q_r is the specific discharge at the point of observation well location (at a distance r from the injection well); r_{ow} is the radius of the observation well; ξ is the correction (skin) factor accounting for additional flow captured by the open well (Shestakov 1995; Novakowski 1992; Zlotnik and Logan 1996). The values of ξ can vary from 0 (fully mudding well) to 2 (no skin effect).

The left-hand part of (8.56) reflects the accumulation of tracer mass in the watered volume of the well during time dt , and the right-hand part is the difference between the tracer masses carried into and out of the well during the same time dt . Formula (8.56) can be written in a dimensionless form:

$$2\alpha \frac{\partial \bar{C}_w}{\partial \bar{t}} = (\bar{C} - \bar{C}_w), \quad (8.57)$$

where α is a *delay (mixing) factor*,

$$\alpha = \frac{\pi r_{ow}}{2\xi r\phi}, \quad (8.57a)$$

which combines the two effects, mixing in the well and the skin factor. On the other hand, the ratio $r_{ow}\xi^{-1}/r\phi$, entering (8.57a), can be considered as the ratio of the effective storage capacity of the measurement system (well) to the storage capacity of the horizon tested within the zone (radius) of influence of the experiment, r .

Laplace transform leads to the linear relationship

$$\tilde{C}_w = \frac{1}{1 + 2\alpha\bar{p}}\tilde{C}, \quad (8.58)$$

relating the concentrations in the formation and the well; here $\bar{t} = t/t_0$, $\bar{p} = pt_0$. From here, it follows that, if the solution for concentration $\bar{C}$ in the bed is known, the solution for the concentration in the well can be readily obtained as a convolution integral

$$\bar{C}_w = \frac{1}{2\alpha} \int_0^{\bar{t}} \exp\left(-\frac{(\bar{t}-\tau)}{2\alpha}\right) \bar{C}(\tau) d\tau. \quad (8.59)$$

To evaluate the time lag effect in testing *homogeneous single porosity rocks*, one can use an approximate solution of the two-dimensional radial microdispersion problem (Sect. 8.1.3), in particular, the solution (8.22)/(8.26) (see Fig. 8.9). The character of the breakthrough curves is in good agreement with the physical concepts (Mironenko and Rumynin 1979). Thus, an increase in r (a decrease in the dimensionless parameter α) leads to a decline in concentration growth rate on the outer wall of the well; therefore, the concentration has enough time to equal to the concentration in the aquifer, i.e., the effect of time lag decreases. An increase in porosity has a similar effect: the capacities of the tested volume of aquifer, $\sim \pi\phi m(r^2 - r_w^2)$, and observation well, $\sim \pi m r_w^2$, become closer. Finally, the invasion of drilling mud into the near-well region ($\xi < 2$) leads to a slower rate of increase in tracer concentration in the well; the delay factor, α , increases, having its

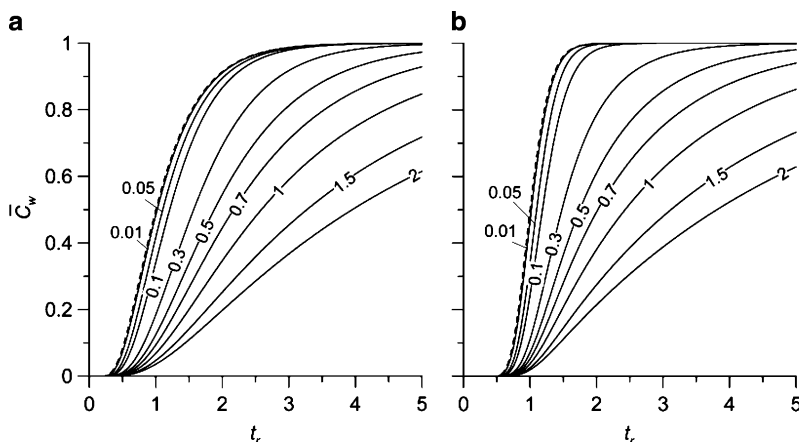


Fig. 8.9 The influence of the magnitude of the delay factor related to the observation well, α , on the breakthrough curves (microdispersion in divergent flow). (a) $Pe = r/\delta_L = 10$, (b) $Pe = 50$. Figures at curves are the values of α . Dashed lines correspond to observation well with no response delay

effect on the character of the breakthrough curves: they become flatter. When α is large, the effect of hydrodynamic dispersion (microdispersion) on the character of breakthrough curves is completely shadowed by the lag effect of the well, as can be seen from the comparison of two plots in Fig. 8.9.

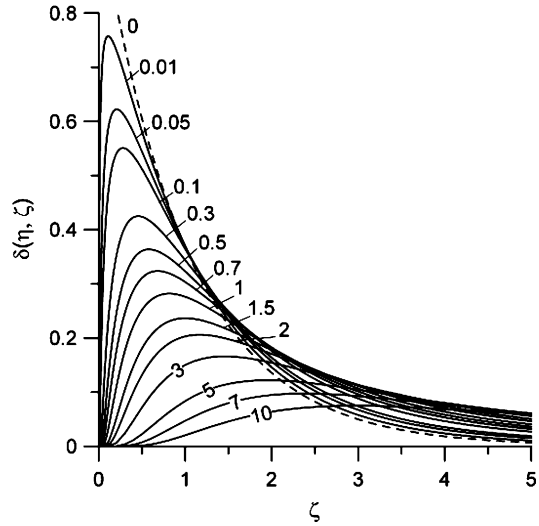
At the same time, the analysis of curves shows that the neglect of the lag effect leads to an appreciable overestimation of the values of porosity (fracture ratio) and microdispersivity. For example, the method of statistical moments (Roshal 1981) can be used to show that errors in estimates of active porosity, ε_ϕ , and dispersivity coefficient, ε_δ , are of the order of α and $2\alpha^2 r/\delta_L$, respectively. Obviously, the lag effect is significant for a low porosity aquifer, and commonly should not be neglected in fractured rocks (where mostly $\alpha > 0.5 - 1$): the errors in parameter estimates can be as large as several hundreds percent. The same is true for observation wells with low values ($\xi < 0.5$) of correction (skin) factor in dispersed (granular) type of the sediments, where the lag effect is especially large in the assessment of microdispersivity.

Analogous estimates for *fractured-porous aquifer* can be obtained by combining formulas (8.59) and (8.33):

$$\bar{C}_w = \int_0^\varsigma \exp[-(\varsigma - \tau)] \operatorname{erfc}\left(\sqrt{\frac{\eta}{4\tau}}\right) d\tau, \quad (8.60)$$

$$\eta = \frac{B_m t_0}{2\alpha}, \quad \varsigma = \frac{(\bar{t} - 1)}{2\alpha}. \quad (8.60a)$$

Fig. 8.10 A plot of the well-influence function, $\delta_w(\eta, \zeta)$. Figures at the curves are the values of the dimensionless parameter η ; the *dashed* line is the curve of tracer dilution in the well in the course of its migration in a fractured reservoir with very low mass exchange characteristics of porous matrix, $\eta \rightarrow 0$ ($B_m \rightarrow 0$)



The solution (8.60) can also be written as (Rumynin 1981)

$$\bar{C}_w = \bar{C}(\eta, \zeta) - \delta_w(\eta, \zeta), \quad (8.61)$$

allowing two components to be isolated: the first is the concentration function for a well without lag effect

$$\bar{C}(\eta, \zeta) = \operatorname{erfc}\left(\sqrt{\frac{\eta}{4\zeta}}\right), \quad (8.61a)$$

and the second component is the function of influence of the well $\delta_w(\eta, \zeta)$, see Fig. 8.10. As can be readily seen from (8.61), in an observation well with pronounced lag effect, the observed concentration variations lag behind the solution (8.33) by the time $\delta_w(\eta, \zeta)$.

It is easy to show that, within a wide range of experimental characteristics, the lag effect results in an appreciable overestimation of the fracture ratios and mass exchange parameters of blocks. The maximal errors in the estimates of active fracture ratio in rocks with low lumped mass transfer coefficient are of the order of the values of α . When

$$\eta = \frac{\lambda_m \phi_m^2 \xi m r^3}{r_{ow} Q_w} > 5, \quad (8.62)$$

the errors drop to 15–20%, however, only if experimental data characterizing breakthrough curve where $\bar{C} > 0.2 - 0.3$ are used. At the same time, from modeling analysis it follows that, unlike experiments in homogeneous fractured aquifers (with negligibly small matrix diffusion), the influence of time lag effects on test results in fractured-porous aquifers with increased mass transfer coefficients can be appreciably smoothed by purposeful variations in experimental characteristics (injection rate, the distance between wells) (Mironenko and Rumynin 1986).

8.3.2 Effect of Tracer Dilution in the Source Well

The above-considered solutions for the interpretation of experiments in radially convergent flow created by a pumping-out well (Sect. 8.2), were based on the assumption that a short-term (theoretically, impulse-like) tracer injection into an aquifer is carried out using a well, often, using one of the piezometers belonging to a multi-well aquifer test system. However, under actual field conditions, the tracer is mixing with water in the source well-casing and then gradually is washed out from the well filter by ambient flow. Therefore, the input signal in the form of Dirac delta function is not a proper approximation for the input boundary condition (Welty and Gelhar 1994; Zlotnik and Logan 1996; Mironenko and Rumynin 1998b; Chen et al. 2002; 2003; Brouyère et al. 2005). The effect under consideration can be associated with the time lag of injection (input) well.

This type of boundary condition is often approximated by a simple formula (Welty and Gelhar 1994)

$$C_w(t) = \frac{M}{V_{ow}} \exp\left(-\frac{t}{t_w}\right), \quad (8.63)$$

which can be regarded as a solution of Eq. 8.57, with $C = C^0 = 0$ (tracer concentration in the ambient water) and $C(t = 0) = M/V_{ow}$; here V_{ow} is solution volume in the well,

$$t_w = \frac{V_{ow}}{Q_{ow}} = \frac{\pi r_{ow}^2 m}{2\xi r_{ow} m (Q_w / 2\pi R m)} = 2\alpha t_0, \quad \alpha = \frac{\pi r_{ow}}{2\xi R \phi}; \quad (8.63a)$$

Q_{ow} is the volumetric rate of the transit flow passing through the well; $t_0 = \pi m \phi R^2 / Q_w$. Note that the process of dilution, as was the case with tracer tests in divergent flow, is governed by the dimensionless parameter α , delay (in this context, dilution) factor. A more strict representation of the boundary condition on the contour of the injection (source) well may require the duration and rate of tracer solution injection into the well to be taken into account (Brouyère et al. 2005).

The general solution of the problem can be represented in the integral dimensionless form

$$\bar{C}(\bar{t}, \zeta_i, \alpha) = \frac{1}{2\alpha} \int_0^{\bar{t}} \exp\left[-\frac{(\bar{t} - \tau)}{2\alpha}\right] \bar{C}(\tau, \zeta_i) d\tau, \quad (8.64)$$

Similar to (8.59); here the function $\bar{C}(\tau, \zeta_i)$ corresponds to one of the known solutions obtained for a pulse input, e.g., the solution (8.52e) in the case of an experiment in homogenous rocks ($\zeta_i \equiv \text{Pe}$), see Fig. 8.11, a, or the solution (8.55) for testing a fractured-porous reservoir ($\zeta_i \equiv \bar{\lambda}$, $\text{Pe} = 0$), see Fig. 8.11b ($\bar{t} = t/t_0$).

Calculations show (Fig. 8.11), that for the effect under consideration to appreciably influence the character of the breakthrough curves, the coefficient α should be greater than 0.05–0.1. Such situation is most realistic in fractured-rock complexes,

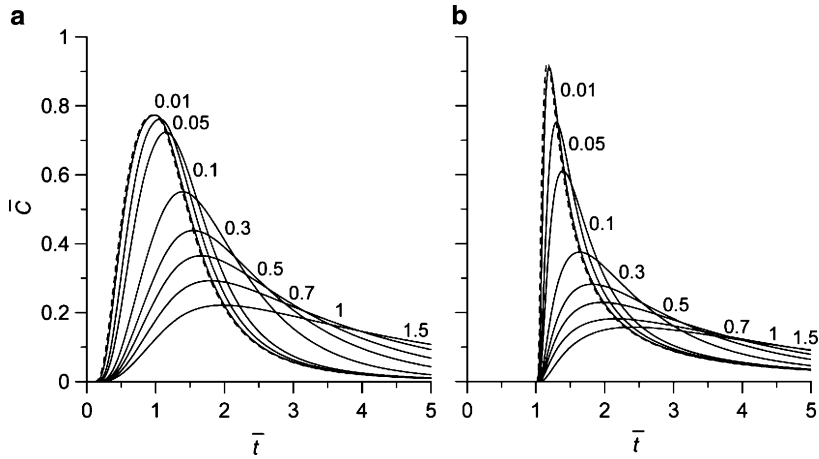


Fig. 8.11 The influence of the tracer dilution in the source well on the breakthrough curves. (a) Single porosity reservoir ($Pe=10$), (b) fractured-porous reservoir ($\lambda=1$). Figures at curves are the values of delay (dilution) factor, α . The *dashed* curves are for a well without lag effect (pulse injection)

where parameter ϕ varies within 10^{-3} – 10^{-4} . Overall, as can be seen from Fig. 8.11, the neglect of tracer dilution in the source well in the interpretation of experiments results in overestimation of porosity, microdispersivity, and mass transfer coefficient. Especially large errors should be expected when low-quality wells with high correction (skin) factor are involved.

8.4 Analytical Models for Doublet Tracer Testing

A doublet configuration of tracer experiment acts as a source-sink system, including injection/recharge and extraction/pumping wells. In optimum experimental setting, the recharge and pumping rates are set to be identical. A tracer is added to the recharge water as a step increase, a square pulse of a concentration parcel, or a pulse of a finite tracer mass. A doublet test may be carried out in a non-recirculating or recirculating tracer input mode with respect to repetitive use of *tracer-labeled* water extracted from the discharge well for its re-injection into the recharge well. The main disadvantage of the doublet tracer test is in difficulties of data analysis (Grove and Beetem 1971; Mironenko and Rumynin 1986; Hydraulic and tracer testing..., 1996). In a doublet flow field, the travel time from the recharge well to the pumping well varies over the streamline along which the tracer travels. Thus, the shape of the breakthrough curve is primarily controlled by the different travel times of the tracer along different streamtubes and not by the dispersion in each streamtube, and, consequently, the effect of dispersion is not as evident as in the divergent or convergent tracer tests (Hydraulic and tracer testing..., 1996).

8.4.1 Flow Field and Travel Time Between Recharge and Discharge Wells

The groundwater flow network formed by two interacting wells (recharge and discharge) is two-dimensional and planar (Fig. 8.12a). The description of the migration process can be simplified if one, neglecting the effect of hydrodynamic dispersion, transforms the initial Eq. 1.5 into complex potential domain and considers solute transport along fixed flow lines ψ in a quasi-one-dimensional formulation (see Sect. 1.2.2).

With well layout shown in Fig. 8.12a, the equations of flow lines, ψ , and potential function, φ , become (Hoopes and Harleman 1967b; Grove and Beetem 1971; Novakowski et al. 1985)

$$\varphi = \frac{Q_w}{2\pi m} \operatorname{arcth} \left[\frac{2dx}{d^2 + (x^2 + y^2)} \right], \quad \psi = \frac{Q_w}{2\pi m} \operatorname{arctg} \left[\frac{2dy}{d^2 - (x^2 + y^2)} \right]; \quad (8.65)$$

with the specific discharge

$$q(\varphi, \psi) = \frac{Q_w}{2\pi md} \left[\operatorname{ch} \left(\frac{2\pi m \varphi}{Q_w} \right) + \cos \left(\frac{2\pi m \psi}{Q_w} \right) \right]; \quad (8.66)$$

here $2d$ is the distance between the wells; Q_w is the volumetric discharge/recharge rate of the pumping/injection well.

With such representation of the flow, the values of function ψ , varying between 0 and $Q_w/2m$, characterize the shares of fluid flow entering the well along different flow bands (lying between the shortest flow line $\psi = 0$ and the flow line with the current value of ψ); the values of function φ vary from $+\infty$ (on the contour of the

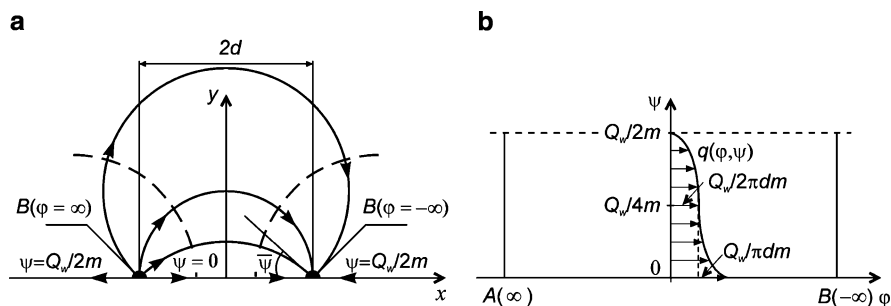


Fig. 8.12 Illustration to solute migration in the flow field created by recharge and discharge wells. (a) Schematic diagram showing equipotentials and streamlines for a doublet-well system in the upper half-plane (A and B are the recharge and discharge wells, respectively; *dashed* lines show equipotential contours, $\varphi = \text{const}$; *full* lines show streamlines, $\psi = \text{const}$); (b) the representation of groundwater flow in the $\psi - \varphi$ plane; *arrows* show the Darcy velocity profile, having a “sinusoidal” character (see Eq. 8.66)

recharge well) to $-\infty$ (on the contour of the discharge well). Geometrically, the flow domain is the rectangle $-\infty < \varphi < \infty$, $0 \leq \psi \leq Q_w/2m$ in the system of curvilinear coordinates (φ, ψ) (see Fig. 8.12b).

Any flow line ψ (upper half plane) has a time characteristic $t(\psi)$, equal to the time required for a liquid particle to move through the appropriate trajectory (Hoopes and Harleman 1967b; Grove and Beetem 1971; Charbeneau 2000):

$$t_0(\psi) = \phi \int_{+\infty}^{-\infty} \frac{d\varphi'}{q^2(\psi, \varphi')} = \frac{\pi(2d)^2 m \phi}{Q_w} \left(\frac{\sin \bar{\psi} - \bar{\psi} \cos \bar{\psi}}{\sin^3 \bar{\psi}} \right) \equiv t_0(\bar{\psi}), \quad (8.67)$$

where $\bar{\psi} = 2\pi m \psi / Q_w$ ($0 \leq \bar{\psi} \leq \pi$) is the angle between the tangent to the flow line in the center of the discharge well and the positive direction of the x -axis (Fig. 8.12a).

The length of the curvilinear trajectory $L(\bar{\psi})$ is

$$L(\bar{\psi}) = \frac{2d\bar{\psi}}{\sin \bar{\psi}}. \quad (8.67a)$$

When $\bar{\psi} = 0$ (the shortest flow line), $t_0 = 4\pi d^2 m \phi / 3 Q_w$ (this is twice the migration time from the midpoint between wells to the discharge well, see formula 1.89). Conversely, for any time $t = t_0$, there exists a value of flow function $\psi_0 = \psi(t_0)$ (and the appropriate angle $\bar{\psi}_0$), whose absolute value corresponds to half the discharge of the tracer-containing liquid entering the discharge well at time t_0 . Essentially, (8.67) is a characteristic solution of the initial differential equation (1.76).

Given the (arbitrary) orientation of the doublet axis relative to the principal axes of hydraulic-conductivity anisotropy, an expression for the characteristic time $t'_0(\psi)$, analogous to (8.4), can be written as (Konosavsky et al. 1993):

$$t'_0(\bar{\psi}) = \frac{4\pi m d^2 \phi (\cos^2 \varphi + \kappa^2 \sin^2 \varphi)}{\kappa Q_w} \cdot \frac{\sin \bar{\psi} - \bar{\psi} \cos \bar{\psi}}{\sin^3 \bar{\psi}}, \quad (8.67b)$$

where φ is the angle between the doublet axis and the minimal permeability direction. For the shortest flow line ($\bar{\psi} = 0$), we have

$$t'_0 = \frac{4\pi m \phi d^2 (\cos^2 \varphi + \kappa^2 \sin^2 \varphi)}{3 \kappa Q_w}. \quad (8.67c)$$

8.4.2 Piston-Like Tracer Displacement in a Homogeneous Single Porosity Aquifer

The formulation of the problem given above allows one to take into account the different time of solute reaching the discharge well via different trajectories and its mixing with the formation water containing no solute. This can be made using an integral representation of the solute concentration in the well:

$$C(t) = \frac{2m}{Q_w} \int_0^{Q_w/2m} C(t, \psi) d\psi, \quad (8.68)$$

where $C(t, \psi)$ is solute concentration entering the discharge well via flow line ψ at moment t . The mixing formula (8.68) represents the concentration as the ratio of the specific flux of solute mass entering the well to its discharge per unit formation thickness.

When the solution of the boundary-value problem can be obtained in the form of function $C(t, t_0)$ of two arguments – the current time t and the characteristic time of the process t_0 (see formula (8.67)), the relationship (8.68) can be written in the following dimensionless form:

$$\bar{C}(t) = \frac{1}{\pi} \int_0^\pi \bar{C}(t, t_0) d\bar{\psi} = \frac{1}{\pi} \left(\int_0^{\bar{\psi}^*} \bar{C} d\bar{\psi} + \int_{\bar{\psi}^*}^\pi \bar{C} d\bar{\psi} \right). \quad (8.69)$$

The solution (8.69) is basic for *non-recirculating tracer input mode*. Thus, proceeding from a purely advective transport ($\bar{C} = 1$ at $0 \leq \bar{\psi} \leq \bar{\psi}^*$ and $\bar{C} = 0$ at $\bar{\psi}^* < \bar{\psi} \leq \pi$), we have

$$\bar{C}(t) = \frac{\bar{\psi}^*(t_0)}{\pi}; \quad (8.70)$$

here $\bar{C}(t) = C(t)/C_0$; $\bar{\psi} = 2\pi m\psi/Q_w$ is the angle of the flow line sector delivering the tracer into the discharge well (see Fig. 8.12a); $\bar{\psi}^*(t_0)$ determines the extreme of such lines at moment $t = t_0$. For any time moment t , the angle $\bar{\psi}^*$ can be found from the transcendent formula (8.67). It can be seen from here that the character of variations in the concentration function is governed by the value $(2d)^2 m\phi/Q_w$.

The solution (8.70) can be approximated, with an error of no more than 1%, by the formula (Konosavsky et al. 1993):

$$\bar{C}(t) = \frac{2}{\pi} \arccos \left(\frac{t_0}{t} \right)^{1/\pi}, \quad t \geq t_0 = \frac{\pi(2d)^2 m\phi}{3Q_w}; \quad (8.71)$$

in the general case of an anisotropic formation, the time t_0 is determined by (8.67b). This formula is convenient, in particular, for the construction of solutions taking into account heterogeneous (in terms of concentration) boundary conditions.

Thus, Fig. 8.13 gives plots corresponding to a *square-pulse input*, whose duration, t_s , is a multiple of the characteristic time scale ($\bar{t}_s = t_s/t_0 = 1, 2, 3, 4, 5$). An important feature is the abrupt asymmetry of the plots, which manifests itself in large gradients of the concentration function $\bar{C}(t)$ on descending branches.

The following figure (Fig. 8.14) reflects another particular result, corresponding to calculating the concentration function for *recirculating input tracer mode*. In this scenario, it is assumed that in the initial period of doublet scheme operation, the water injected through the recharge well contains a constant boundary concentration, $\bar{C}$.

Fig. 8.13 The character of breakthrough curves for doublet tracer test in the case of a square-pulse of a concentration input. Figures at the curves are the values of the ratio t_s/t_0

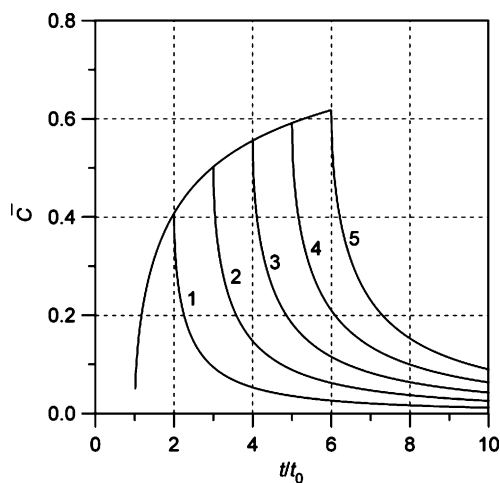
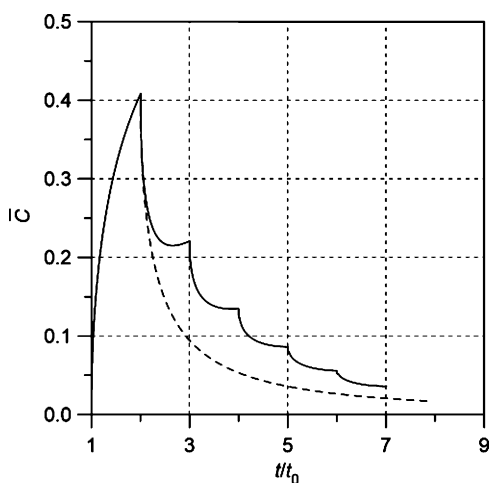


Fig. 8.14 Plot of the normalized concentration function, $\bar{C}(\bar{t})$. The *full* line is for the recirculation scheme, the *dashed* line is a solution for a square pulse of a concentration input. $\bar{t}_s = 1$



Next, at moment $t = t_0$, when the first portion of solute appears in the discharge well, the solute supply is ceased and the input concentration at all subsequent stages of the test coincides with the breakthrough concentration function $\bar{C}(t)$. As seen from Fig. 8.14, the superposition of successive concentration waves disturbs the monotonicity of the descending branch of the resulting plot (it was constructed by using a multilevel superposition of solution (8.71)), and the time coordinate of each local peak corresponds to a multiple of t_0 . Note that the implementation of such, fully closed, scheme in a doublet experiment enables the tracer to be used more efficiently.

The variants of solution construction considered above can be extended to the analysis of migration in heterogeneous (dual porosity) systems (see Sect. 8.4.4).

8.4.3 An Approximate Solution for Microdispersion in a Homogeneous Aquifer

A streamline-based approach is used to construct such solution. The main computation relationship for the doublet scheme is the first equality in (8.69), where the integration function $\bar{C}(t, t_0)$ is the solution of microdispersion equation in quasi-one-dimensional formulation

$$\bar{C}(t, t_0) \approx \frac{1}{2} \operatorname{erfc} \left(\frac{t_0 - t}{\sqrt{2\sigma_t^2}} \right), \quad (8.72)$$

and the time $t_0 = t_0(\psi)$ is determined by (8.67); here σ_t^2 is a parameter characterizing the deviation of the actual motion time t of tracer-marked particles from the time t_0 ; this parameter can be estimated at $\sigma_t^2 \approx 2 t_0 t \delta_L / L(\bar{\psi}) = 2 t t_0 \sin \bar{\psi} / (\bar{\psi} \text{Pe})$ ($L(\bar{\psi})$ is the length of the flow line (8.67a), $\text{Pe} = 2d/\delta_L$ is the characteristic *Peclet* number; $\bar{\psi} = 2\pi m \psi / Q_w$). The solution (8.72) is a concise form of Sauty's solution (1980), describing tracer migration along an arbitrary trajectory, where the distance L is assumed to be covered by the piston-type front during time t_0 .

The plot of the dimensionless concentration function (Fig. 8.15), where the dimensionless time $\bar{t} = 3Q_w t / 4\pi d^2 m \phi$ corresponds to the absolute time t , standardized with respect to the time of tracer motion along the shortest flow line, $t_0(\bar{\psi} = 0)$, for different Pe values can be used as typical in the interpretation of migration test results. As follows from the analysis of the plot, variations in the concentration in the record well are largely determined by the tracer reaching the well at different moments along different flow lines. This hampers the determination of the dispersion characteristics of the formation (the sensitivity of the test curves to these characteristics is very low, especially in the range of relative concentrations, $\bar{C} > 0.2$), but yields a more reliable averaged estimate of porosity (fracture ratio)

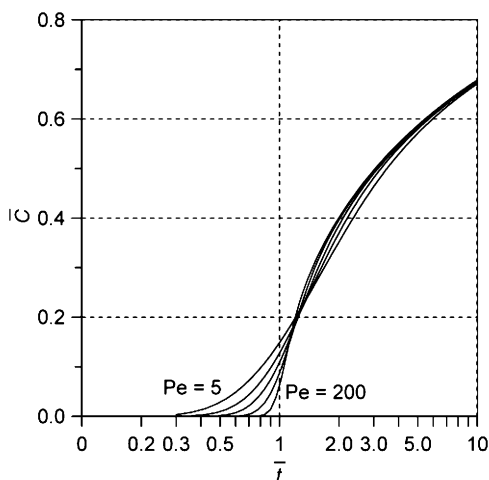


Fig. 8.15 Theoretical calibration curves, $\bar{C}(\bar{t})$, for model of microdispersion at $\text{Pe}=5, 10, 20, 50, 200$

8.4.4 Solutions for Mass Transfer in a Fractured-Porous Aquifer

The streamline-based approach in this case involves the use of generalized solutions (6.24)/(6.40a) and (6.31)/(6.40b), corresponding to the schemes of unlimited and lumped storage capacity in the case of piston-like motion of tracer in fractures. The concentration in the discharge well can be found by averaging over all flow lines in accordance with the integral solution (8.69), where the characteristic time $t_0(\psi)$ is determined from (8.67); in the numerical integration, one should take into account that for $t < t_0$, we have $\bar{C}(t, t_0) = 0$. The typical plots (Figs. 8.16 and 8.17) are of use for the analysis of the process.

Fig. 8.16 Theoretical calibration curves, $\bar{C}(\bar{t})$, for unlimited matrix diffusion model. Figures at curves are the values of $\bar{\lambda}$, $t_0 = 4\pi d^2 m \phi / 3Q_w$

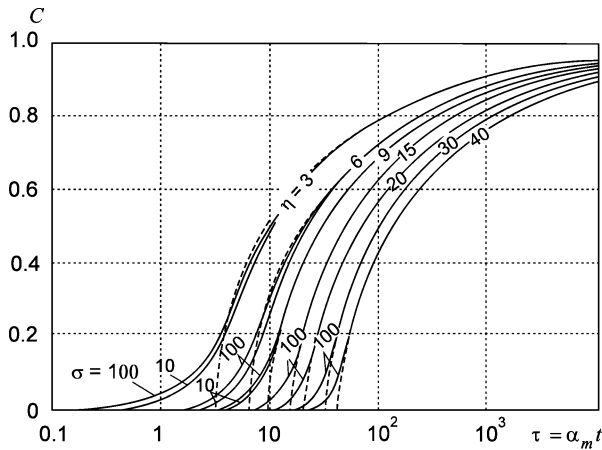
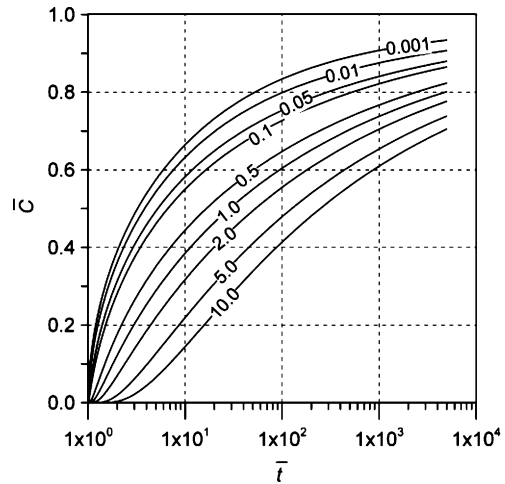


Fig. 8.17 Theoretical calibration curves, $\bar{C}(\tau)$, for first-order mass transfer model. Figures at curves are the values of parameters η and σ ; dashed lines are for piston-like displacement model, neglecting exchange process kinetics

The first plot (Fig. 8.16), corresponding to the unlimited capacity model, depends on two dimensionless groups

$$\bar{\lambda} = B_m t_0, \quad \bar{t} = \frac{t}{t_0} \quad \text{at} \quad t_0 = \frac{4\pi d^2 m \phi}{3Q_w}. \quad (8.73)$$

With $\bar{\lambda} \rightarrow 0$ (when the formation is composed of porous blocks with very low mass exchange characteristics) the curve corresponds to the solution (8.70) for piston-like displacement scheme in a homogeneous medium. When $\bar{\lambda} > 0.3 - 0.4$, as is the case for a wide range of experiments with electrolytic tracer in dual porosity media with high mass exchange characteristics, the breakthrough curves in the interval $0.1 < \bar{C} \leq 0.5$ are well approximated by a logarithmic function (Rumynin and Mironenko 1996)

$$\bar{C}(t) \approx -\frac{1}{2} \log(\xi), \quad \xi = \frac{\sqrt{\bar{\lambda}}}{2} \sqrt{\frac{t_0}{t - t_0}}. \quad (8.74)$$

This yields a quite reliable estimate of parameter B_m ; conversely, the sensitivity of the breakthrough curves to active fracture ratio, ϕ , becomes extremely low.

The theoretical tracer concentration curves, $\bar{C} = \bar{C}(\tau)$ ($\tau = \alpha_m t$), for the lumped capacitance model (Fig. 8.17) depend on the dimensionless groups $\eta = 4\alpha_m \phi_m m d^2 / Q_w$ and $\sigma = \phi_m / \phi$. From here it follows that the interaction kinetics between fractures and porous matrix is appreciable only at the initial segments of breakthrough curves ($\bar{C} < 0.2 - 0.3$), while $\tau < \eta$. Otherwise, as well as at $\eta > 30 - 40$ (for all τ), the first-order mass transfer coefficient, α_m , is almost indeterminable, i.e., lumped capacitance model is less sensitive to errors in mass exchange coefficient assessment. In this case, the curve $\bar{\lambda} = 0$ (Fig. 8.16) can be used for calculations with $\phi \equiv \phi_m$. When α_m and (or) the distance between wells are sufficiently large (at about $\eta > 5$) the breakthrough curves are insensitive to active fracture ratio parameter, ϕ .

8.5 Problems Related to the Subvertical Migration of Tracers in a Field of Recharge and Discharge Wells

8.5.1 Problem Conceptualization

There are some common situations where we would expect mass transport in groundwater to proceed essentially in the vertical direction, perpendicular to the bedding planes of water-bearing formations. Thus, a dense plume of industrial waste or brine, initially located in the lower part of thick water-bearing formations, starts moving vertically (downwards or upwards) because of the density contrast between groundwater and liquid waste or water table drawdown associated with pumping

from water intake wells. To predict the gravity effects related to the plume sinking scenarios and the processes controlling the displacement of brackish and fresh water interface in a thick formation, some field tests with artificial or natural tracers can be utilized. The other typical problem which can require studying the aquifer properties in both horizontal and vertical directions concerns the development of in situ remediation (physical or biological) technique using vertical circulation flows around wells with several sections screened within the aquifer at different depths (McKnight et al. 2004).

This section focuses specifically on the analysis of two typical situations relating to tracer displacement due to changes in groundwater dynamics caused by discharge and and/or recharge well operations. The former situation (Fig. 8.18) is associated with the displacement of the natural contact between waters with different qualitative characteristics, initially occupying the lower and upper parts of the aquifer. Such displacement takes place under the effect of water withdrawal from a partially penetrating well with a screen section of a finite length l , adjacent to the roof of

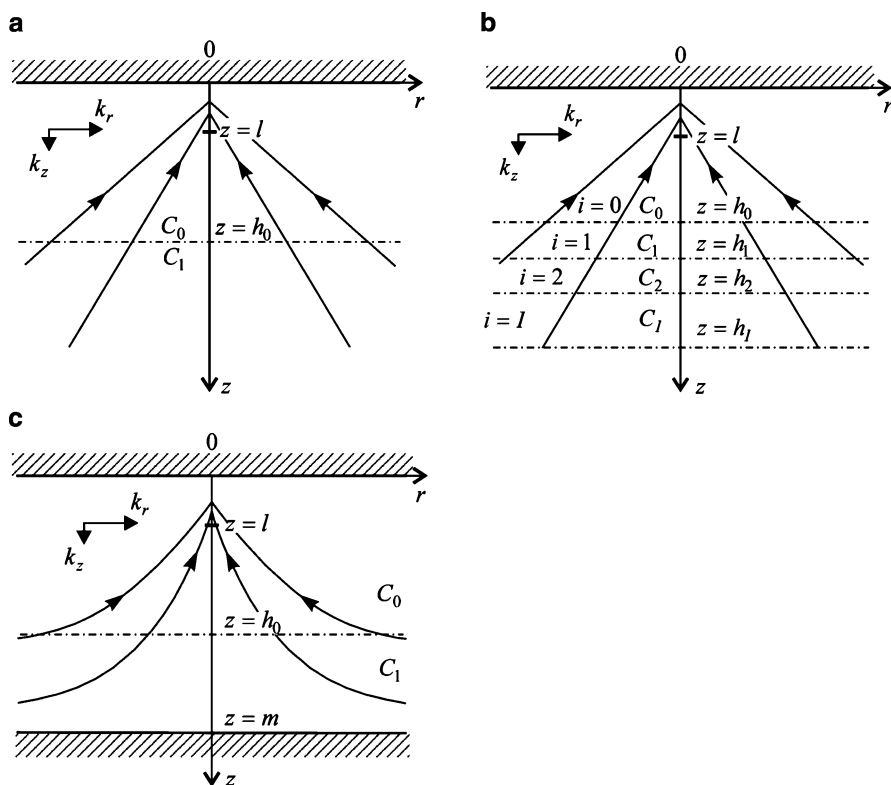


Fig. 8.18 Schematic sketches showing conceptually the subvertical cross formation flow in the zones of influence of partially penetrating wells. (a) A discharge well in a semibounded confined aquifer in the case of a sharp interface between two water-bearing zones with different concentrations of a dissolved component, C_1 and C_2 ; (b) a discharge well in a semibounded confined aquifer in the case of nonuniform solute distribution, C_i , within the transition zone; (c) a discharge well in a confined aquifer of limited thickness

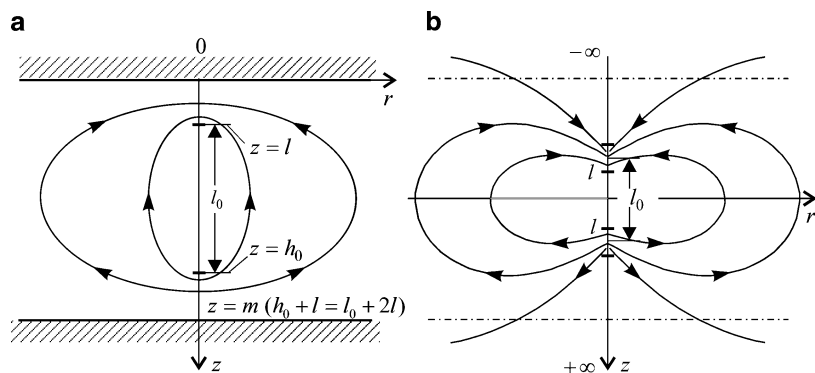


Fig. 8.19 Schematic sketches showing conceptually the vertical dipole experimental setting. (a) A pair of dipole wells in a confined aquifer of limited thickness; (b) a pair of dipole wells in an aquifer of unlimited thickness

the formation (Fig. 8.18). The need to solve such problems arises during the assessment of groundwater quality formation at water intakes, which excessively disturb the natural groundwater salinity stratification in the ground through uncontrolled well pumping. The latter situation (Fig. 8.19) is associated with describing tracer migration between two wells (discharge and recharge), whose screen intervals are located one beneath the other. A single well, equipped with packers for separating the injection and extraction sections, can also be used (Sutton et al. 2000; McKnight et al. 2004; Chen et al. 2010). Such dipole (doublet) systems are used in experimental studies of permeability and migration parameters of rocks that control solution migration in the subvertical direction.

Of primary interest are calculation relationships describing (1) the time required for the first portions of solute (tracer) to reach the upper screened interval in the aquifer ($0 \leq z \leq l$) along the shortest flow line from the interface between waters of different quality ($z = h_0$, Fig. 8.18), or from the screen-section of tracer injection (Fig. 8.19); (2) variations in solute (tracer) concentration ($\bar{C}$, dimensionless concentration) in the discharge well interval (screen section). The effect of hydrodynamic dispersion is commonly shadowed by the variations in the time required for the solute to reach the discharge well along flow lines in a heavily deformed groundwater flow network; therefore, it is reasonable to consider the migration process under the assumption of piston-like displacement. If the solution density difference is not taken into account, the mathematical constructions will be based on steady-state flow equations, supplemented by characteristic (kinematic) equations.

8.5.2 Partially-Penetrating Well Operation Under the Condition of Nonuniform Initial Concentration Profile

The solution for a well in a homogeneous, semibounded (in the vertical section), anisotropic formation with a horizontal initial interface (Fig. 8.18a) at depth h_0

between waters with different concentrations, C , of some marker component (C_0 in the top layer and C_1 in the bottom layer), has the form (Kisel and Abramov 1978)

$$\bar{C}(t) = 1 - \frac{f_0}{\beta}, \quad (8.75)$$

where $\bar{C}(t) = [C(t) - C_0]/(C_1 - C_0)$, and the function $f_0 \equiv f(0, \bar{t})$ can be found from the transcendent formula

$$\bar{t} = \beta \kappa^2 \left[\frac{(1 - f_0^3) \beta^2}{f_0^3} - 3f_0(1 - f_0) \right]. \quad (8.76)$$

The solution (8.75)–(8.76) is valid under the condition

$$\bar{t} > \bar{t}_0 = \kappa^2(1 + 2\beta^3 - 3\beta^2), \quad (8.76a)$$

where $\bar{t}_0$ is the dimensionless time required for the water interface to reach the well; $\kappa = \sqrt{k_r/k_z}$ is anisotropy coefficient (k_z is the hydraulic conductivity in the vertical direction); $\beta = l/h_0$ (l is screen length); Q_w is the volumetric discharge of the well; $\bar{t} = t/t'_0$; $\bar{t}_0 = t_0/t'_0$;

$$t'_0 = \frac{2\pi\phi h_0^3}{3Q_w} \quad (8.77)$$

is a “normalizing” time characteristic corresponding to the time needed for water interface (C_1/C_0) in an isotropic bed ($\kappa = 1$) to reach a well with a short screen ($\beta = 0$, a point source).

Analysis of plots of $\bar{C}(t)$ (Fig. 8.20) shows that the process in general is very extended in time: a short period of a rapid increase in the concentration is followed by a long period of very slow variations in function $\bar{C}(t)$. The anisotropy of hydraulic conductivity manifests itself in a shift of plots by about k_r/k_z along the $\bar{t}$ axis.

The complete solution, describing the displacement dynamics of the C_1/C_0 interface ($\bar{r}$, $\bar{z}$, $\bar{t}$) is (Kisel and Abramov 1978)

$$\bar{t}(\bar{r}, \bar{z}) = 6\beta\kappa^2 \left[\frac{4(1 - \bar{z}^3)\beta^2\kappa^3}{3M^3} - \frac{M}{4\kappa}(1 - \bar{z}) \right], \quad (8.78)$$

where $M = \sqrt{\bar{r}^2 + \kappa^2(\bar{z} + \beta)^2} - \sqrt{\bar{r}^2 + \kappa^2(\bar{z} - \beta)^2}$, $\bar{r} = r/h_0$, $\bar{z} = z/h_0$ (the author's modification of expression for M). An example of calculations in Fig. 8.21 serves to illustrate the behavior of solution (8.78).

Finally, it can be shown that, when $\beta = 0$, the solution (8.75) becomes

$$\bar{C}(t) = f(t, t_0), \quad (8.79)$$

$$f(t, t_0) = 1 - \left(\frac{t_0}{t}\right)^{1/3}, \quad t_0 = \kappa^2 t'_0 = \frac{2\pi\kappa^2\phi h_0^3}{3Q_w}, \quad (8.80)$$

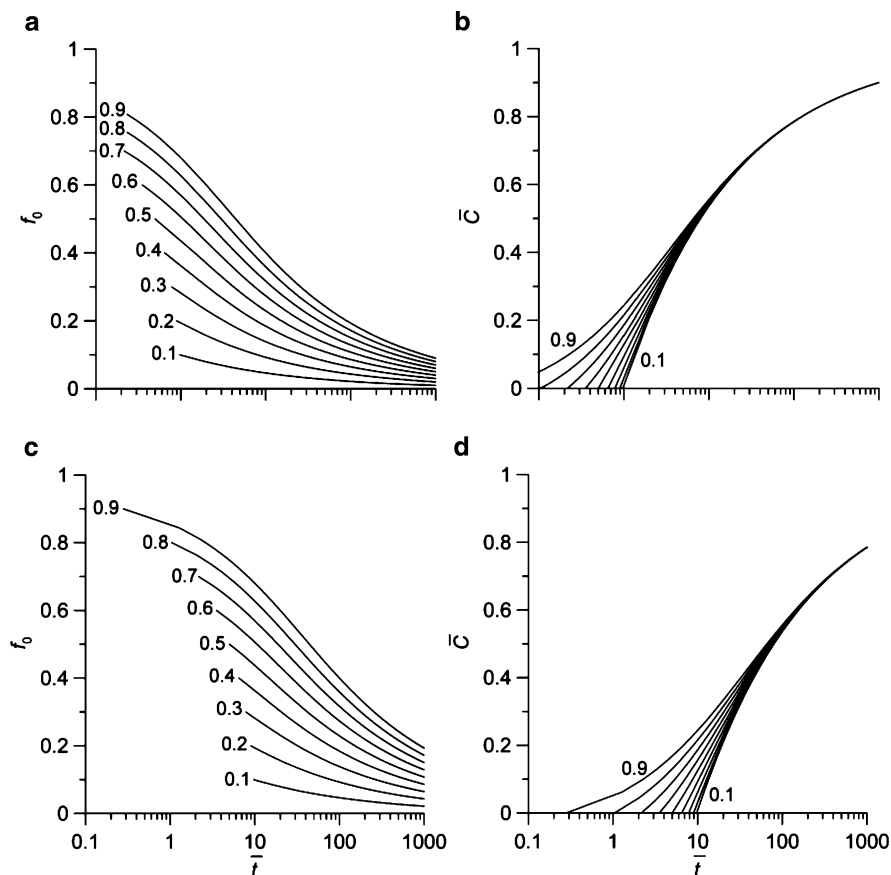


Fig. 8.20 Plots of functions f_0 (a, c) and $\bar{C}$ (b, d) for solute transport in (a, b) an isotropic ($\kappa = 1$) and (c, d) an anisotropic ($\kappa = \sqrt{10}$) formation. Figures at the curves are the values of parameter β

or, expressed in the absolute values of concentration,

$$C(t) = C_0 + (C_1 - C_0)f(t, t_0). \quad (8.81)$$

Analysis of the solution obtained for calculating $\bar{t}_0$ for wells in a formation (aquifer) with a limited thickness (Goldberg 1976) shows that the effect of aquifer bottom on the value of $\bar{t}_0$, calculated by (8.77), certainly neglected when the thickness, h_0 , of the top water layer (with the tracer concentration C_0) does not exceed half the thickness, m , of the aquifer.

In aquifers of limited thickness, the process at a sufficiently large distance from the water intake can be assumed planar (Fig. 8.18c). The solution of an appropriate boundary value problem for a point-wise water intake is plotted in Fig. 8.22, where $\bar{h}_0 = h_0/m$, $t_m = 2\pi m^3 \phi / Q_w$ (Konosavsky et al. 1993). When $\bar{h}_0 \leq 0.5-0.6$, this

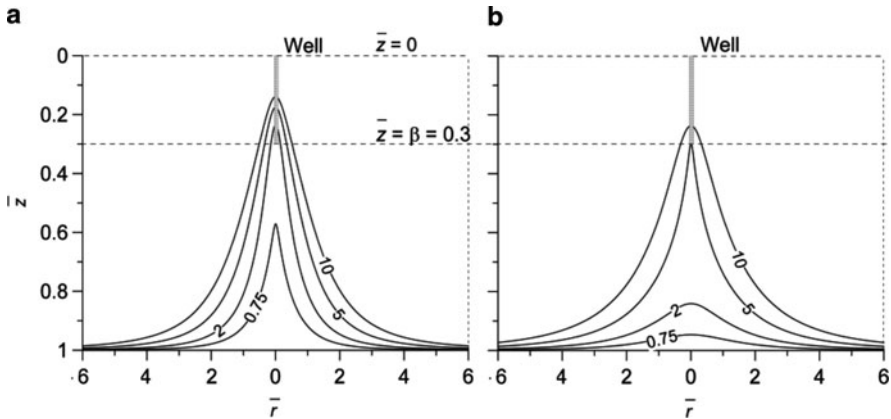


Fig. 8.21 Advancing interface C_1/C_0 below a pumping well as a function of dimensionless spatial coordinates, $\bar{z}$ and $\bar{r}$, and time, $\bar{t}$ (figures at the curves), solution (8.78). (a) An isotropic formation, $\kappa = 1$; and (b) an anisotropic formation, $\kappa = \sqrt{5}$

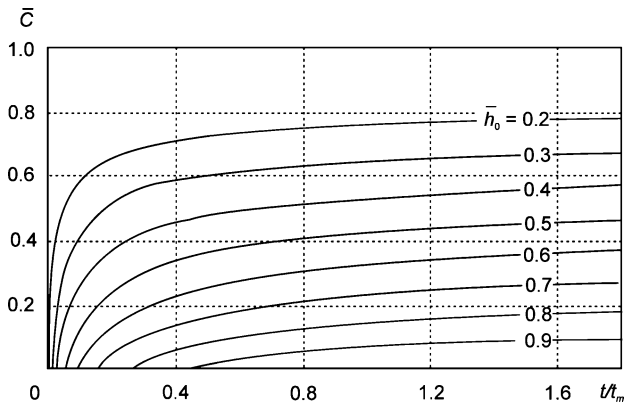


Fig. 8.22 Plot of the normalized concentration function, $\bar{C} = f(t/t_m)$, for subvertical migration in an aquifer of limited saturated thickness

solution can be approximated with an error less than 5–7% by relationships (8.79) and (8.81) with (Mironenko and Rumynin 1986)

$$f(t, t_0) \approx (1 - \bar{h}_0) \left[1 - \left(\frac{t_0}{t} \right)^\alpha \right], \quad \alpha = 3^{(\bar{h}_0 - 1)}, \quad t \geq t_0 = \frac{\kappa^2 \bar{h}_0^3 t_m}{3}. \quad (8.82)$$

In the presence of a transition zone from fresh to mineralized water (Fig. 8.18b), a superposition of solutions of the type of (8.75) and (8.81) is used. Thus, for a well with a short screen ($\beta = 0$) in a semi-bounded (in cross-section) aquifer, in accordance with (8.81), we have

$$C(t) = C_0 + \sum_1^I (C_i - C_{i-1}) f(t, t_{i-1}), \quad (8.83)$$

where I is the number of the bottom model layer ($I + 1$ is the total number of layers with constant concentration, C_i , approximating variations in component concentrations over aquifer thickness); i is the current layer's number ($i = 0$ for the top layer with the background concentration C_0), see Fig. 8.18b; t_{i-1} is the time when mineralized waters start entering from the top boundary of the i th model layer at the depth of h_{i-1} ; it is defined by the second formula in (8.80), where h_0 is to be replaced by h_{i-1} .

Formula (8.83) with

$$f(t, t_{i-1}) \approx (1 - \bar{h}_i) \left[1 - \left(\frac{t_{i-1}}{t} \right)^{\alpha_{i-1}} \right], \quad \alpha_{i-1} = 3^{(\bar{h}_{i-1}-1)}, \quad \bar{h}_i = \frac{h_i}{h_I} \quad (8.84)$$

is also valid for the upconing process in aquifers of limited thickness ($h_I \equiv m$). The characteristic time t_{i-1} is calculated by the second formula (8.80); when $t < t_{i-1}$, we have $f(t, t_{i-1}) = 0$.

The density-induced convection, caused by a density gradient at the interface between waters in the top and bottom zones of the groundwater reservoirs, is a factor that appreciably shifts the estimates derived from the relationships considered here. The effect of this factor on the migration process as a whole is discussed in Sects. 12.3 and 14.2.

8.5.3 Plots and Formulas for the Analysis of Vertical Dipole Tests

This type of aquifer testing is mostly intended for studying the parameters governing the efficiency of rehabilitation of polluted areas by using wells to create active cross-bedding circulation water flows. Flow problem solutions (Kabala 1993; Zlotnik and Ledder 1996; Communar 2000) form the basis for the analysis of the hydrodynamic structure of the flow, which has an appreciable vertical component of Darcy velocity. Flow problem solution allows one to obtain expressions for flow lines connecting the separated (by casing or packers) recharge and discharge screen-intervals of wells. Numerical integration along these lines makes it possible, in particular, to calculate the characteristics $t_0(s)$ and $\omega(t)$ (1.138a), entering the generalized solution (1.96)/(1.139)/(1.140) for the subsequent numerical-and-analytical evaluation of the concentration function (Sutton et al. 2000). Also possible is the search for a solution of the problem incorporating pore velocity components, u_r and u_z , taken from a known analytical solution of the flow problem, in an advection–dispersion equation written in cylindrical coordinates (Chen et al. 2010). Some physical assumptions, simplifying problem formulation, allow approximate relationships to be obtained in analytical closed-form solutions. In our analysis, only the advective component of transport is taken into account.

8.5.3.1 Homogeneous Single Porosity Aquifer

Suppose that the injection and extraction screen sections of the well are adjacent to the aquifer boundaries in the vertical section (Fig. 8.19a). The origin of coordinate coincides with the discharge well, the z -axis is directed along doublet axis.

If the screen sections of the well are approximated by point sources and a sink ($l = 0$), the migration time along an arbitrary flow line can be calculated as

$$t = \frac{\phi}{k_z} \int_m^0 \frac{dz}{\partial s(r, z)/\partial z}, \quad (8.85)$$

where $s(r, z)$ is the head drawdown function, derived from the solution of the flow problem. The equation of flow lines, along which integration is being carried out, has the form (Konosavsky et al. 1993)

$$\begin{aligned} & \frac{\bar{z}}{\sqrt{\kappa^{-2}\bar{x}^2 + \bar{z}^2}} + \sum_{i=1}^{\infty} \left\{ \frac{2i + \bar{z}}{R(2i + \bar{z})} - \frac{2i - \bar{z}}{R(2i - \bar{z})} + \frac{2i - 1 - \bar{z}}{R(2i - 1 - \bar{z})} - \frac{2i - 1 + \bar{z}}{R(2i - 1 + \bar{z})} \right\} \\ & = \frac{1}{\sqrt{1 + \kappa^{-2} \operatorname{tg}^2 \psi}}, \end{aligned} \quad (8.86)$$

where $\bar{z} = z/m$, $\bar{x} = x/m$, $R(\bar{y}) = \sqrt{\kappa^{-2}\bar{x}^2 + \bar{y}^2}$, $\kappa = \sqrt{k_r/k_z}$; ψ is the central angle between the flow line and the z -axis in the sink; m is the aquifer thickness.

The law of mixing yields the following expression for tracer concentration in the discharge well

$$\bar{C}(t) = \frac{Q_\psi}{Q_\pi} \equiv 1 - \frac{1}{\sqrt{1 + \kappa^{-2} \operatorname{tg}^2 \psi}}, \quad (8.87)$$

where $Q_\pi = Q_w/2$, Q_ψ is the rate of flow into the well from the zone bounded by flow lines forming angle ψ in the discharge well.

Given the value $\bar{C} = \bar{C}(t)$ ($t \geq t_0$, t_0 is the travel time along the shortest flow line), we can find from (8.87) the central angle ψ , corresponding to the outermost flow line in the Eq. 8.86, limiting the sector through which the solute-bearing water enters the well. The record moment of $\bar{C}$ in the pumped-out water can be found from Eq. 8.85, where the integral is taken along the flow line with the central angle ψ (Konosavsky et al. 1993).

Concentration function for a point sink/source pair, $\bar{C}$, depends only on the dimensionless time, $\tau = Q_w t / \pi m^3 \phi$, and aquifer flow anisotropy, κ^2 . For the input *step pulse* function it can be approximated by a breakthrough curve of the form

$$\bar{C}(t) \approx 1 - \left(\frac{\tau_0}{\tau} \right)^n, \quad \tau \geq \tau_0, \quad (8.88)$$

where $\tau_0 = \tau_0(\bar{l} = 0) \approx 0.135\kappa^2$ is the dimensionless travel time along the shortest flow line connecting the source and the sink ($r = 0$); $n = 1/2$. Figure 8.24 indicates a

good agreement between analytical approximation (8.88) and modeling results (see below). The error of the approximate solution (8.88) does not exceed 5% at $\bar{C} \geq 0.1$.

Obviously, the solution of the tracer transport problem under consideration in a closed-form is useful since it allows one to investigate the behavior of experimental breakthrough curves for different forms of the input concentration functions and flow conditions. Thus, one can easily show that the differentiation of function (8.88), according to (1.123), yields a solution for *Dirac pulse* (instantaneous injection of solute mass, M)

$$C_i = \frac{M}{V} \frac{n}{\bar{\tau}^{n+1}}, \quad \bar{\tau} = \tau/\tau_0 \geq 1, \quad (8.89)$$

where $V = \pi m^3 \phi / 6$ is the volume of rock void space between the injection and discharge sections involved in tracer transport of solute input. Analytical formula (8.89) can be used for planning tracer tests and preliminary parameter assessments, as is confirmed by numerical modeling (Fig. 8.23a). Due to the manifestation of the numerical dispersion, the initial and near-peak parts of the model curve are smoothed out. The same tendency can be expected from the influence of physical dispersion of the tracer front in a tested aquifer (Sutton et al. 2000; Chen et al. 2010).

Another solution can be obtained for a *square input pulse* basing on superposition of two basic functions (8.88) (written for τ and $\tau - \tau_s$), according to (1.125). The results are plotted in Fig. 8.23b.

The long tailing in both plots (Fig. 8.23) seems to be induced by a strong spatial deformation of the flow lines between the injection and extraction borehole intervals resulting in different tracer residence times.

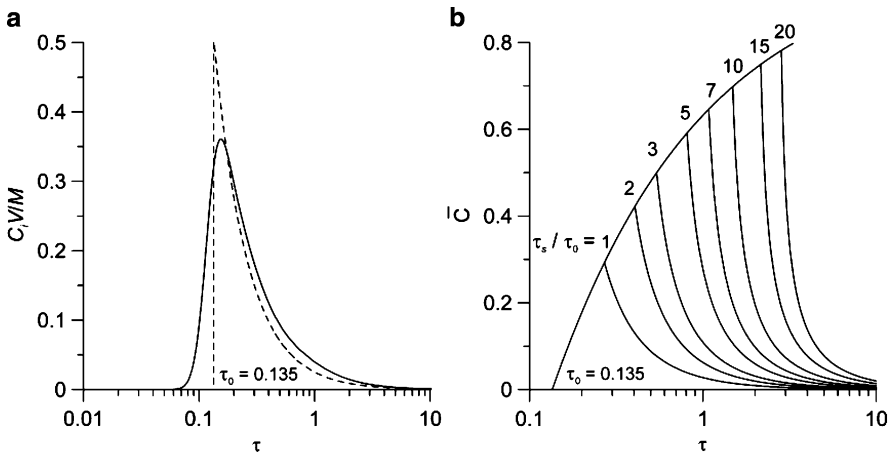
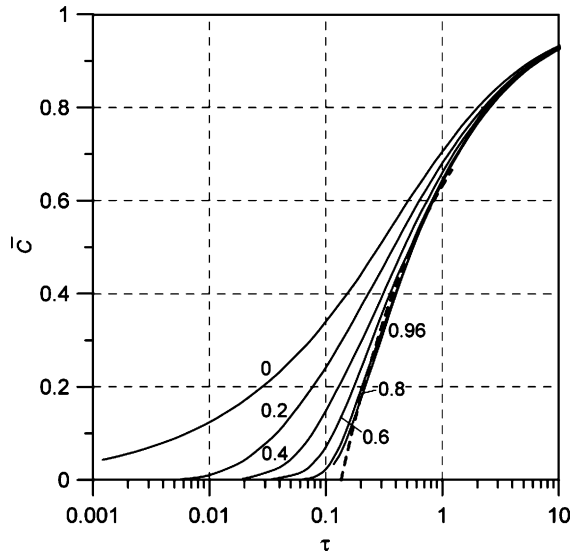


Fig. 8.23 Behavior of the concentration function for two types of the basic input pulses (an isotropic aquifer, $\kappa = 1$). (a) Dirac delta pulse (*solid* curve is numerical model data, *dash* curve is approximate solution (8.89)); (b) square pulse for different dimensionless input step duration, τ_s

Fig. 8.24 Breakthrough curves (finite-element solution of 2D advection equation in cylindrical coordinates using TOUGH2 simulator), $\bar{C}(\tau, \bar{l}_0)$, for a vertical dipole system (figures at the curves are the dimensionless distances between the screen interval inner edges, $\bar{l}_0 = 1 - 2\bar{l}$; $\tau = Qt/\pi m^3 \phi$). Dash curve corresponds to analytical approximation (8.88) for $\bar{l}_0 = 1$ ($\bar{l} = 0$)



The complete solution of the problem for a well with two screen sections of equivalent finite length can be represented as a plot of typical breakthrough curves (Fig. 8.24). Note that the initial part of the curves ($C \leq 0.1$) may be slightly affected by numerical dispersion).

A closed-form analytical approximation for the time of particle travel along the straight line between the screen sections is as follows

$$\tau_0 = (\kappa^2 \bar{l}_0 / e)^{1.7}, \quad (8.90)$$

where $\bar{l}_0 = 1 - 2\bar{l}$; e is the base of natural logarithm. Relationship (8.90) is valid for $\bar{l} \geq 0.2$.

Finally, consider a dipole system in an unbounded (in cross-section) homogeneous aquifer (Fig. 8.19b). Similar to the previous experimental set-up, typical breakthrough curves were obtained using numerical modeling approach. One may note that the concentration curves in dimensionless coordinates, $\bar{C} - \tau$ (Fig. 8.25), tend to the asymptotic curve associated with the point source and sink more quickly in comparison with a bounded in profile aquifer (Fig. 8.24).

Concentration function for a point sink/source pair, $\bar{C}$, depending only on the dimensionless time, $\tau = Q_w t / \pi l_0^3 \phi$, and aquifer flow anisotropy, κ^2 , can be accurately approximated by a simple formula (8.88), where $\tau_0 \approx 0.25 \kappa^2$ and $n = 1/4$ (Fig. 8.26a). Then application of solution (8.89), assuming $V = \pi l_0^3 \phi / 6$, allows one to describe the behavior of the concentration function as a response to instantaneous injection of a finite mass of indicator in the recharge section of the well (Fig. 8.26b).

Fig. 8.25 Breakthrough curves (finite-element solution of 2D advection equation in cylindrical coordinates using TOUGH2 simulator), $\bar{C}(\tau, \bar{l})$, for a vertical dipole system (figures at the curves are the dimensionless screen sections' length, $\bar{l} = l/l_0$; $\tau = Qt/\pi l_0^3 \phi$; l_0 is the distance between the centers of the screen sections)

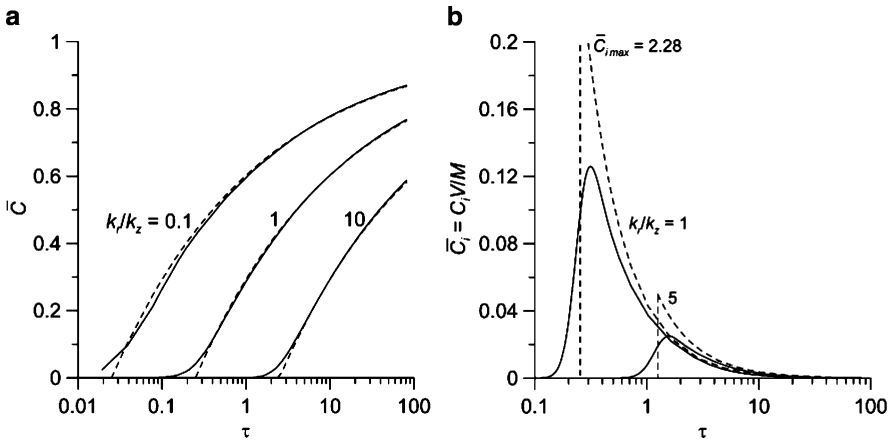
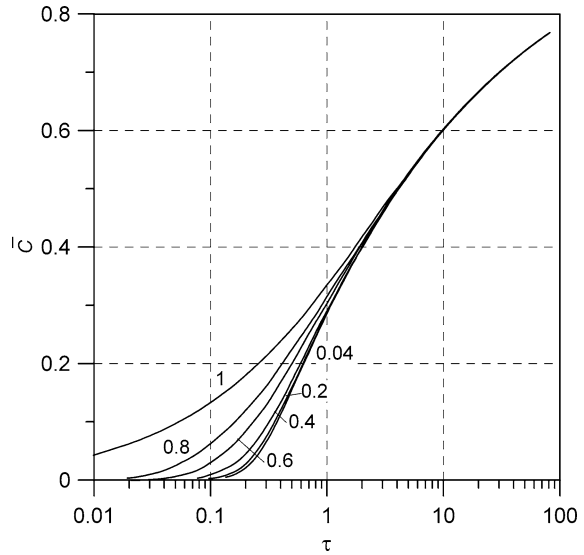


Fig. 8.26 Comparison of numerical solutions of the dipole tracer test problem (solid curves) against analytical approximate formulas (8.88) and (8.89) (dash curve) for the two basic input pulses. (a) Square pulse, (b) Dirac delta pulse

8.5.3.2 Fractured-Porous Aquifer

Only the advection flow component and solute exchange between fractures and blocks are taken into account. The general solution has the form (Konosavsky et al. 1993)

$$\bar{C}(t) = \frac{1}{Q_\pi} \int_0^{Q_\psi^*} \bar{C}_i(t, t_\psi) dQ_\psi, \quad (8.91)$$

where Q_{ψ^*} is the rate of inflow into the well from the zone bounded by the flow lines forming in the discharge well a central angle ψ^* at moment t ; t_{ψ} ($< t$) is the migration time along the flow line with a central angle ψ ; the origin of coordinates coincides with the discharge well; the z -axis is directed along the axis of the doublet. Well screens are approximated by point sources and sinks. The concentration function $\bar{C}_i(t, t_{\psi})$, $i=1, 2$, is defined by one of the scale-restricted models of tracer diffusion in porous matrix (see Sects. 6.1.2 and 6.1.3):

- for model of unlimited matrix diffusion

$$\bar{C}_1(t, t_{\psi}) = \operatorname{erfc} \left(\frac{\sigma \lambda_m^{1/2} t_{\psi}}{2 \sqrt{t - t_{\psi}}} \right), \quad (8.91a)$$

- for lumped-capacitance (first-order transfer kinetics) model

$$\bar{C}_2(t, t_{\psi}) = 1 - e^{-\tau_{\psi}} \int_0^{\eta_{\psi}} e^{-z} I_0(2\sqrt{\tau_{\psi} z}) dz \quad (8.91b)$$

with $\eta_{\psi} = \sigma \alpha_m t_{\psi}$, $\tau_{\psi} = \alpha_m (t - t_{\psi})$.

We write (8.91) as

$$\bar{C}(t) = \int_0^{\psi^*} f'(\psi) \bar{C}_i(t, t_{\psi}) d\psi, \quad (8.92)$$

where $f'(\psi) = (1/Q_{\pi})(dQ_{\psi}/d\psi)$.

For vertical doublet experimental setting in an aquifer with unlimited thickness, we have

$$\frac{Q_{\psi}}{Q_{\pi}} = \frac{1}{2} \left[1 - \frac{\operatorname{sgn}(\cos \psi)}{\sqrt{1 + \kappa^{-2} \operatorname{tg}^2 \psi}} \right] \approx 1 - (t_0/t_{\psi})^{1/4}. \quad (8.93)$$

From here we obtain an equation for function $f'(\psi)$:

$$f'(\psi) = \operatorname{sgn}(\cos \psi) \frac{\kappa^{-2} \operatorname{tg} \psi / \cos^2 \psi}{2(1 + \kappa^{-2} \operatorname{tg}^2 \psi)^{3/2}}; \quad (8.94)$$

where the angle ψ^* at the moment t is found from the condition (8.93):

$$t = t_{\psi^*} = \frac{16 t_0}{\left\{ 1 + \frac{\operatorname{sgn}(\cos \psi^*)}{\sqrt{1 + \kappa^{-2} \operatorname{tg}^2 \psi^*}} \right\}^4}, \quad (8.95)$$

where $t_0 = 4\kappa^2 m^3 \phi / 3\pi Q_w$. Thus, the solution (8.92) can be readily integrated by numerical methods and used to analyze tracer transport in a fractured-porous

aquifer where exchange between fracture and matrix solutions is described in the framework of different asymptotic models for dual porosity reservoirs (see Sects. 6.1.2 and 6.1.3).

The formulas given above clearly do not cover the entire diversity of experimental conditions; therefore, one often has to use numerical solution to analyze migration processes in subvertical flows by means of mathematical modeling.

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Chapter 9

Models for Prediction of Effects of Pumping on Groundwater Quality at Well-Fields

Traditionally, hydrogeological research into the effects of changes in groundwater quality has focused on the influence of industrial and/or agricultural near-surface sources of contamination on the subsurface environment. However, in water supply systems (wellfields), the change in *hydraulic conditions* due to pumping can, on its own account, become a hazard to the water quality. Thus, water withdrawal from a well or a well cluster creates a potential for vertical (upward or downward) migration of water with specific ion or isotope composition through or from neighboring hydrogeological units to the water-producing aquifers, resulting in degradation of the pumped groundwater quality. The relevant analytical models, describing the shift in the depth stratification of water quality in interconnected aquifers (leaky aquifer systems) under the influence of groundwater withdrawal, supplement a set of models predicting the saltwater upconing towards the pumping wells due to freshwater abstraction (see Sects. 8.5, 12.3, and 14.2.3). Water quality degradation within the aquifers where vertical leakage is induced by hydraulic-head differences was observed in many wellfields under exploitation all over the world (Goode et al. 1993; El-Bihery and Lachmar 1994; Foster and Chilton 2003; Marandi and Vallner 2010).

Another negative effect on groundwater quality can result from the lowering of groundwater table. Indeed, pumping causes changes in the *geochemical conditions* in the soil above the cone-like depression of the piezometric surface by opening access of atmospheric oxygen, which oxidizes sulphides, thus increasing the concentrations of sulphates and dissolved heavy metals, which move downward with recharge water to the producing aquifer (Larsen and Postma 1997; Appelo and Postma 2005; Lekhov and Vishnyak 2005).

9.1 Change in the Groundwater Quality in Leaky Aquifer Systems

There are two major scenarios (or conceptual schemes) for releasing “environmental” dissolved solutes to the producing aquifer (Fig. 9.1). The first scenario is associated with migration of water with an increased content of dissolved solids or water containing industrial (or environmental) tracers from an adjacent aquifer through an incompressible semipervious bed to a water-producing aquifer. Thus,

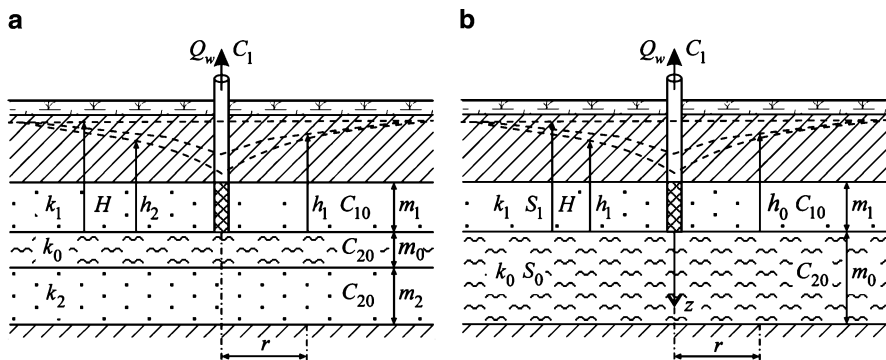


Fig. 9.1 Water pumping from a bed receiving additional recharge: (a) leakage through the separating bed from the adjacent aquifer, (b) squeezing out of water from the underlying bed

the relevant model is useful to predict the water quality in a lower aquifer which is affected by leakage of water from the polluted upper phreatic aquifer due to the water level drawdown in the lower aquifers. The second scenario is associated with squeezing of pore water of specific composition out of the underlying (or overlying) semipervious compressible bed to the producing layer.

The described physical models can be simplified as: (a) *a two-aquifer system*, which consists of an upper and a lower confined aquifers with a leaky stratum between them (Fig. 9.1a), and (b) *a two-layer system*, which consists of a semipervious bed (layer) which responds to the production from an adjoining permeable layer (aquifer) by developing a time-variant flux of water into the pumping aquifer (Fig. 9.1b). Hydrogeochemical response to the pumping will be associated with changes in the concentration, C , of a reference solute (component) – a nonreactive stable tracer. We also assume that in a leaky aquifer system under consideration, before pumping, the reference solute has a known initial concentration (C_{10} and C_{20}) as it is shown in Fig. 9.1.

9.1.1 Flow and Mass Balance Equations

Suppose that the input of components into an aquifer tapped by a well is only due to crossflow, i.e., leakage of water with different composition from an adjacent aquifer (Fig. 9.1a) or elastic squeezing of interstitial water from the underlying bed (Fig. 9.1b). After a certain period the drawdown due to pumping approaches quasi-steady-state, during which heads vary in space-time while gradients (determining the advective flux) vary only in space. Under these conditions the general mass balance equation for a solute transport in the pumped aquifer (convergent radial flow) has the form

$$m_1 \phi_1 \frac{\partial C_1}{\partial t} + m_1 \frac{1}{r} \frac{\partial}{\partial r} [q_1(r) C_1] - q_0(r) C_{20} = 0, \quad (9.1)$$

where $C_1 = C_1(r, t)$ is the current concentration of the reference solute in a point, r , within the aquifer from which water is being withdrawn; C_{20} is the concentration of the solute in the adjacent aquifer and separating beds, which is assumed to be constant; m_1 and ϕ_1 are the thickness and porosity of the main aquifer; $q_1(r)$ is the horizontal component of specific discharge in the production aquifer (in the case of radial convergent flow, it is directed against r -axis, $q_1 < 0$); $q_0(r)$ (> 0) is the vertical rate of flow through the separating beds.

By differentiating with respect to the space coordinate, Eq. 9.1 can be modified as follows

$$m_1 \phi_1 \frac{\partial C_1}{\partial t} + m_1 q_1 \frac{\partial C_1}{\partial r} + m_1 \left(\frac{1}{r} q_1 + \frac{\partial q_1}{\partial r} \right) C_1 - q_0 C_{20} = 0. \quad (9.2)$$

In a particular case of steady state the continuity equation for radial flow takes the form

$$T_1 \frac{1}{r} \frac{d}{dr} \left(r \frac{dh_1}{dr} \right) + q_0 = 0, \quad (9.3)$$

where $T_1 = k_1 m_1$. This, with $q_1 = -k_1 dh_1/dr = k_1 ds_1/dr$ ($s_1 = H - h_1$, Fig. 9.1) yields

$$\frac{m_1}{r} \frac{d}{dr} (r q_1) = m_1 \left(\frac{1}{r} q_1 + \frac{\partial q_1}{\partial r} \right) = q_0. \quad (9.4)$$

Now the base mass balance Eq. 9.2 can be transformed to the form

$$\frac{\partial C_1}{\partial t} + u \frac{\partial C_1}{\partial r} + \varepsilon (C_1 - C_{20}) = 0, \quad (9.5)$$

or

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial r} + \varepsilon C = 0, \quad (9.6)$$

where $C = C_1 - C_{20}$, $u = u(r) = q_1(r)/\phi$, $\varepsilon = \varepsilon(r) = q_0(r)/m_1 \phi_1$.

In the general case, with the depletion of aquifer storage reserves taken into account, we have

$$S_1 \frac{\partial h_1}{\partial t} = T_1 \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial h_1}{\partial r} \right) + q_0, \quad (9.7)$$

where S_1 is the storage coefficient of the main aquifer [—]; $S_1 = S_{s1} m_1$; S_{s1} is the specific storage [L^{-1}]. Now

$$\frac{m_1}{r} \frac{\partial}{\partial r} (r q_1) = q_0 - S_1 \frac{\partial h_1}{\partial t}, \quad (9.8)$$

and Eq. 9.2 takes the form

$$\frac{\partial C_1}{\partial t} + u \frac{\partial C_1}{\partial r} + \varepsilon (C_1 - C_{20}) - \frac{S_1}{m_1 \phi_1} \frac{\partial h_1}{\partial t} C_1 = 0. \quad (9.9)$$

As Eq. 9.9 is implicitly based on a quasi-steady-state assumption for horizontal flow in the main aquifer, a given formalism for the incorporation of a time-dependent

source-term into the mathematical model under consideration is not a fully correct operation and such approach can be treated as a first approximation.

9.1.2 Solutions of Radial Flow Problems

For a two-aquifer system (Fig. 9.1a), the solution of the flow problem, for long pumping periods, in terms of drawdown functions s_1 and s_2 , can be represented in the form (Hantush 1967)

$$s_1 = \frac{Q_w}{4\pi(T_1 + T_2)} \left[\ln \frac{2.25a^*t}{r^2} + \frac{2}{v} K_0 \left(\frac{r}{B} \right) \right], \quad (9.10)$$

$$s_2 = \frac{Q_w}{4\pi(T_1 + T_2)} \left[\ln \frac{2.25a^*t}{r^2} - 2K_0 \left(\frac{r}{B} \right) \right], \quad (9.10a)$$

where Q_w is the rate of water withdrawal; $T_1 (= k_1 m_1)$ and $T_2 (= k_2 m_2)$ are the transmissivities of beds (aquifers); $a^* = (T_1 + T_2)/(S_1 + S_2)$ is the effective (total) hydraulic diffusivity;

$$B = \sqrt{\frac{m_0 T_1 T_2}{k_0 (T_1 + T_2)}}, \quad v = \frac{T_1}{T_2} \quad (9.11)$$

(B is the leakage factor, k_0 and m_0 are the hydraulic conductivity and the thickness of the separating layer); $K_0(z)$ is modified zero-order *Bessel* function of the second kind.

The vertical flow rate q_0 can be found from the obvious relationship

$$q_0 = \frac{k_0}{m_0} (s_1 - s_2) = \frac{Q_w}{2\pi B_1^2} K_0 \left(\frac{r}{B} \right), \quad (9.12)$$

where $B_1 = \sqrt{\frac{m_0 T_1}{k_0}} = B\sqrt{1+v}$. Let us substitute q_0 (which does not depend on time) from Eq. 9.12 into the flow continuity Eq. 9.4 with the latter rewritten as

$$d(rq_1) = \frac{Q_w}{2\pi m_1 B_1^2} K_0 \left(\frac{r}{B} \right) r dr. \quad (9.13)$$

Integrating the left and right parts of Eq. 9.13 yields

$$rq_1 = -\frac{Q_w r B}{2\pi m_1 B_1^2} K_1 \left(\frac{r}{B} \right) + c, \quad (9.14)$$

where $K_1(z)$ is the modified first-order *Bessel* function of the second kind. The integration constant $c = -Q/(2\pi m_1) v/(1+v)$ can be found from

$$\frac{r}{B} \rightarrow 0 \quad q_1 = -\frac{Q_w}{2\pi m_1 r}, \quad K_1\left(\frac{r}{B}\right) = \frac{B}{r}. \quad (9.14a)$$

Finally, we have:

$$q_1 = -\frac{Q_w}{2\pi m_1 r(1+\nu)} \left[\nu + \frac{r}{B} K_1\left(\frac{r}{B}\right) \right]. \quad (9.15)$$

The obtained characteristics of the flow field q_0 and q_1 will allow the mass transport problem to be solved later (see Sect. 9.1.3.1).

For a two-layer system (Fig. 9.1b), where water inflow into the well is due to the depletion of elastic reserves in the high-permeability and low-permeability beds, the solution of the flow problem in terms of the drawdown function (for relatively long water withdrawal periods) has the form (Streltsova 1988):

$$s_1 = \frac{Q_w}{4\pi T_1} \left(-\text{Ei} \left(-\frac{r^2}{4a^*t} \right) \right), \quad (9.16)$$

$$s_0 = s_1 \left\{ 1 - \frac{4}{\pi} \sum_{n=1,3,5,\dots}^{\infty} \frac{1}{n} \exp \left[-\left(\frac{n\pi}{2} \right)^2 \frac{k_0}{S_0 m_0} t \right] \sin \left(\frac{n\pi z}{2m_0} \right) \right\}, \quad (9.16a)$$

where $-\text{Ei}(-z) = \int_z^{\infty} \frac{e^{-x}}{x} dx$ is the integral exponential function; $a^* = T_1/(S_1 + S_0)$ is the effective (total) hydraulic diffusivity, S_1 and S_0 are storage coefficients of the high-permeability and low-permeability beds.

The flow rate q_0 can be found from Darcy's law:

$$q_0 = q_0(z=0) = -k_0 \frac{\partial s_0}{\partial z} \Big|_{z=0}, \quad (9.17)$$

where $s_0 \equiv s_0(r, t) = H - h_0(r, t)$ (Fig. 9.1b). We have:

$$q_0 = \frac{2k_0}{m_0} s_1 \sum_{n=1,3,5,\dots}^{\infty} \exp \left[-\left(\frac{n\pi}{2} \right)^2 \frac{k_0}{S_0 m_0} t \right]. \quad (9.18)$$

The series in Eq. 9.18 converges rapidly; therefore, for large t , when relationship (9.16a) for the drawdown s_1 in the high-permeability layer holds, we can write

$$q_0 \approx \frac{2k_0}{m_0} \cdot \frac{Q_w}{4\pi T_1} \left(-\text{Ei} \left(-\frac{r^2}{4a^*t} \right) \right) \exp \left(-\frac{2k_0}{S_0 m_0} t \right), \quad (9.19)$$

or

$$q_0 \approx \bar{\mu} \alpha_0 \frac{Q_w}{4\pi a^*} \left(-\text{Ei} \left(-\frac{r^2}{4a^*t} \right) \right) e^{-\alpha_0 t}, \quad (9.19a)$$

where $\bar{\mu} = S_0/(S_0 + S_1)$, $\alpha_0 = 2k_0/S_0m_0$. One can readily see that the function $q_0(r, t)$ is nonmonotonic: in any point r it has a maximum in time followed by an attenuation period with the leakage velocity tending to zero (see Sect. 9.1.3.2). This means that the zone of solute input from the separating bed steadily shifts (during water drawdown) from the production well in the direction opposite to the radial flow velocity as the depression cone develops. When moving between this zone and the water intake well, the solution receives no significant salt recharge. As will be seen later, this feature of the solute transport process manifests itself in the character of the breakthrough curve.

Now let us substitute the expressions for functions $s_1 = s_1(r, t)$ and $q_0 = q_0(r, t)$ into the flow balance Eq. 9.8. With simple transformations, we obtain the differential identity:

$$d(rq_1) = \frac{S_1 Q}{8\pi m_1 T_1 t} e^{-r^2/4a^*t} dr^2 + \frac{k_0 Q_w}{4\pi m_0 m_1 T_1} \left(-\text{Ei} \left(-\frac{r^2}{4a^*t} \right) \right) e^{-\alpha_0} dr^2. \quad (9.20)$$

Integrating the left and right parts of this identity from r to 0 with the assumption that $q_1(r \rightarrow 0, t) = -Q_w/2\pi mr$ finally yields

$$q_1(r, t) = -\frac{Q_w}{2\pi m_1 r} \left\{ 1 - (1 - \bar{\mu})(1 - e^{-\xi}) - \bar{\mu}\alpha_0 t e^{-\alpha_0 t} \left[1 - \xi \text{Ei}(-\xi) - e^{-\xi} \right] \right\}, \quad (9.21)$$

where

$$\xi = \frac{r^2}{4a^*t} = \bar{Q} \frac{y}{t} \quad \left(y = \frac{\pi m_1 \phi_1 r^2}{Q_w}, \bar{Q} = \frac{Q_w}{4\pi m_1 \phi_1 a^*} \right). \quad (9.21a)$$

From here one can see that $|q_1(r, t)| \leq Q_w/2\pi m_1 r$, i.e., the processes of elastic water yield from the main aquifer, as well as its squeezing out from the impervious bed reduce the radial flow velocity as compared to the incompressible water flow. This effect is governed by three parameters: $\bar{\mu}$, $\bar{Q}$ and α_0 , as can also be seen from the solution of the solute transport problem (see Sect. 9.1.3.2).

9.1.3 Solution of Solute Transport Problems

9.1.3.1 Two-Aquifer System

The process can be described by the linear first-order partial differential Eq. 9.6. It corresponds to the system of ordinary differential equations

$$\frac{dt}{1} = \frac{dr}{u(r)} = -\frac{1}{\varepsilon(r)} \frac{dC}{C}; \quad (9.22)$$

here, with (9.12) and (9.15),

$$u(r) = -\frac{Q_w}{2\pi m_1 \phi_1 r} \frac{1}{1+v} \left[v + \frac{r}{B} K_1 \left(\frac{r}{B} \right) \right], \quad (9.22a)$$

$$\varepsilon(r) = \frac{Q_w}{2\pi m_1 \phi_1 B_1^2} K_0 \left(\frac{r}{B} \right). \quad (9.22b)$$

Integrating the first equality (9.22),

$$\int_0^t dt = \int_r^{r_w} \frac{dr}{u(r)}, \quad (9.23)$$

we obtain the expression for the time it takes for a water particle to move from a point on the cylindrical surface $r = r(t)$ to point $r = r_w$:

$$t = \int_{r_w}^{r(t)} \frac{dr}{|u(r)|}. \quad (9.24)$$

The integral identity for determining the current concentration C in point $r = r_w$ has the form (see the second Eq. 9.22):

$$\int_{C_{10}}^C \frac{dC_1}{C_1 - C_{20}} = - \int_{r(t)}^{r_w} \frac{\varepsilon(r)}{u(r)} dr. \quad (9.25)$$

Such form implies that the condition $C_1 = C_{10}$ holds at the cylindrical surface $r = r(t)$, which can be determined for any time, t , from Eq. 9.24.

Integrating the left part of identity (9.25) yields the final solution of the problem in the form

$$\bar{C} = \frac{C - C_{10}}{C_{20} - C_{10}} = 1 - \exp \left(- \int_{r_w}^{r(t)} \frac{\varepsilon(r)}{|u(r)|} dr \right), \quad (9.26)$$

or, in the explicit dimensionless form,

$$\bar{C} = 1 - \exp \left(- \int_{\bar{r}_w}^{\bar{r}(t)} \frac{K_0(\bar{r}) \bar{r}}{v + \bar{r} K_1(\bar{r})} d\bar{r} \right), \quad (9.27)$$

where $\bar{r}(\bar{r}_w) = r(r_w)/B$. When calculating variations in concentration in a single well, one may assume $r_w = 0$.

A graphical representation of solution (9.27) (the case $r_w = 0$) is given in Fig. 9.2, where dimensionless time is defined as $\bar{t} = Q_w t / 2\pi m_1 \phi_1 B_1^2$ ($B_1 = \sqrt{T_1 m_0 / k_0}$).

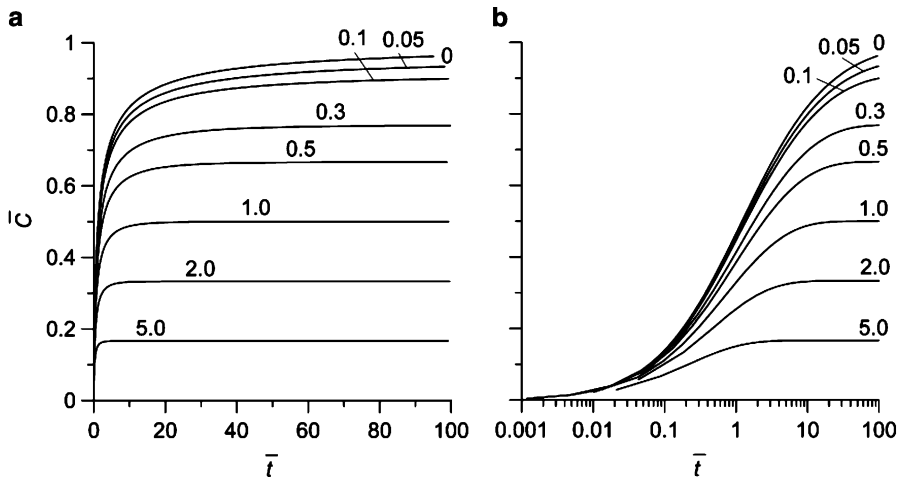


Fig. 9.2 Relative concentrations of a reference solute in pumped-out water (system with leakage): (a) and (b) are for natural and logarithmic scales of dimensionless time. Figures at curves are transmissivity ratios ($v = T_1/T_2$)

As can be seen from the plots, the growth in concentration $\bar{C}$ gradually slows down and this concentration asymptotically tends to the limiting (maximal) value $\bar{C}_{\max}$:

$$\bar{C}_{\max} = \frac{1}{1 + v}, \quad (9.28)$$

depending on the ratio of transmissivities of the interacting aquifers, $v = T_1/T_2$. The time required for the limiting concentration to be attained is typically far in excess of the pumping test duration and comparable with the duration of commercial pumping, if this is carried out from porous aquifers.

In the particular case of infinite water availability in the recharging aquifer ($T_2 \gg T_1$), we obtain

$$\bar{C} = 1 - \bar{r}(\bar{t})K_1[\bar{r}(\bar{t})], \quad \bar{t} = \int_0^{\bar{r}(\bar{t})} \frac{d\bar{r}}{K_1(\bar{r})}, \quad \bar{r} = r/B_1, \quad (9.29)$$

as follows from the tendencies discussed above and coincides with the solution obtained elsewhere (Goode et al. 1993).

9.1.3.2 Two-Layer System

Let us write the original differential Eq. 9.9 as

$$\frac{1}{Q} \frac{\partial C}{\partial \tau} + \bar{u}(\eta, \tau) \frac{\partial C}{\partial \eta} + \bar{E}(\eta, \tau) C + \frac{(1 - \bar{\mu})}{\tau} C_{20} = 0, \quad (9.30)$$

where

$$\bar{u}(\eta, \tau) = - \left\{ 1 - (1 - \bar{\mu})(1 - e^{-\xi}) - \bar{\mu}\tau e^{-\tau} \left[1 - \xi \text{Ei}(-\xi) - e^{-\xi} \right] \right\}, \quad (9.30a)$$

$$\bar{\epsilon}(\eta, \tau) = \bar{\mu} (-\text{Ei}(-\xi)) e^{-\tau} + \frac{(1 - \bar{\mu})}{\tau} e^{-\xi}, \quad (9.30b)$$

$$C = C_1 - C_{20}, \quad \eta = \frac{\pi \alpha_0 m_1 \phi_1 r^2 \bar{Q}}{Q_w}, \quad \tau = \alpha_0 t, \quad \xi = \frac{\eta}{\tau}. \quad (9.30c)$$

The characteristics η and τ are associated with the dimensionless space and time coordinates, respectively.

A complete solution of Eq. 9.30 can be obtained numerically. However, making some simplifying assumptions one can try to obtain a closed-form solution of Eq. 9.30. Thus, the condition $S_0 \gg S_1$ ($\bar{\mu} \approx 1$) holds in most practical cases (the storage coefficient of low-permeability beds, commonly represented by clay rocks, is much greater than the respective characteristic of high-permeability aquifers, which are used for water intake). When $\bar{\mu} = 1$, Eq. 9.30 can be written as

$$\frac{1}{\bar{Q}} \frac{\partial C}{\partial \tau} + \bar{u}(\eta, \tau) \frac{\partial C}{\partial \eta} + \bar{\epsilon}(\eta, \tau) C = 0, \quad (9.31)$$

$$\bar{u}(\eta, \tau) = - \left\{ 1 - \tau e^{-\tau} \left[1 - \xi \text{Ei}(-\xi) - e^{-\xi} \right] \right\}, \quad (9.31a)$$

$$\bar{\epsilon}(\eta, \tau) = -\text{Ei}(-\xi) e^{-\tau}, \quad \bar{Q} = Q_w S_0 / 4\pi T m_1 \phi_1. \quad (9.31b)$$

Functions $\bar{u}(\eta, \tau)$ and $\bar{\epsilon}(\eta, \tau)$ are plotted in Fig. 9.3.

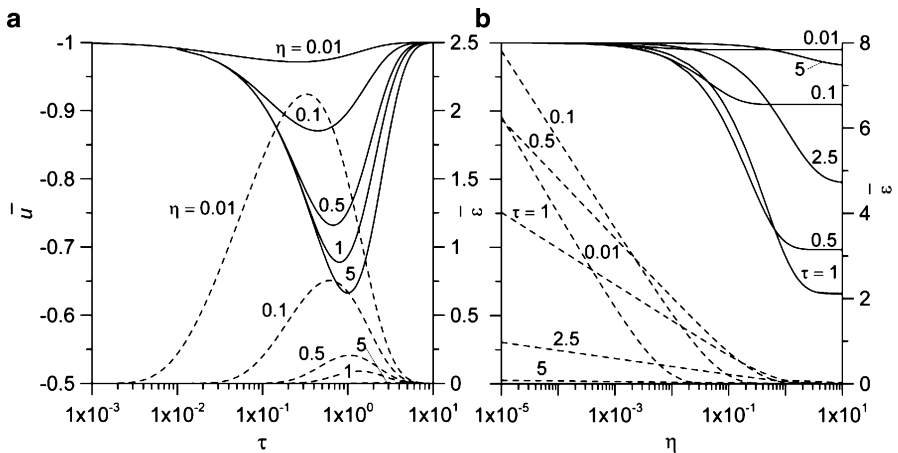


Fig. 9.3 Functions (a) $\bar{u}(\tau)$ (solid lines) and $\bar{\epsilon}(\tau)$ (dashed lines) at fixed η , and (b) $\bar{u}(\eta)$ (solid lines) and $\bar{\epsilon}(\eta)$ (dashed lines) at fixed τ

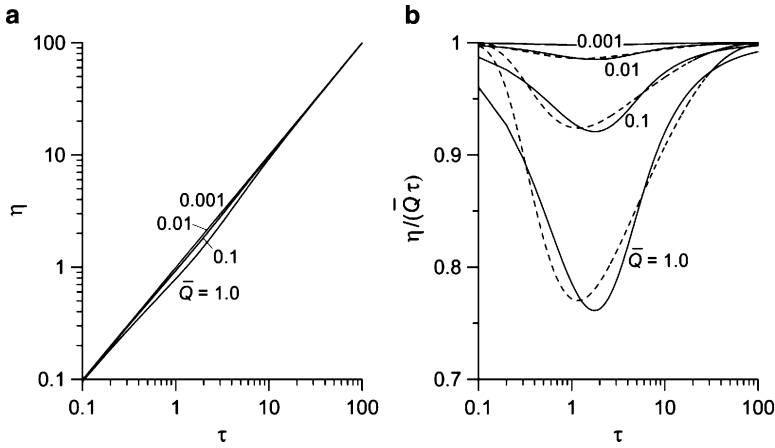


Fig. 9.4 Functions (a) $\eta(\tau)$ and (b) $\eta(\tau)/\bar{Q}\tau$ at different values of dimensionless group $\bar{Q}$

The linear first-order partial differential Eq. 9.31 corresponds to the system of ordinary differential equations:

$$\frac{d\tau}{1/\bar{Q}} = \frac{d\eta(\tau)}{\bar{u}(\eta, \tau)} = -\frac{1}{\bar{\varepsilon}(\eta, \tau)} \frac{dC}{C}. \quad (9.32)$$

The solution of this system of equations by standard numerical procedures made it possible to plot functions $\eta(\tau)$, $\eta(\tau)/\bar{Q}\tau$ (Fig. 9.4), and $\bar{C}(\tau) = (C_1 - C_{10})/(C_{20} - C_{10})$ (Fig. 9.5a).

The nonmonotonic character of plots $\eta(\tau)/\bar{Q}\tau$ (Fig. 9.4b) can be attributed to the extreme behavior of velocity functions $\bar{u}(\eta, \tau)$ and $\bar{\varepsilon}(\eta, \tau)$ (Fig. 9.3a). The obtained curves related to the dynamic ratio $\eta(\tau)/\tau$ can be fitted with the following formula (Fig. 9.4b, dashed curves):

$$\frac{\eta}{\tau} \approx \bar{Q} \left\{ 1 - \frac{a}{\sqrt{\tau}} \exp \left[-\frac{(\tau - c)^2}{b\tau} \right] \right\} = f(\tau), \quad (9.33)$$

where coefficients a , b and c are defined as follows $a = 3.71\bar{Q}^{0.92} - 3.38\bar{Q}$ (for $\bar{Q} \leq 1$), $b = 28.2$, $c = 4.2$. With this approximation, the characteristic η is an analytical function of the dimensionless time

$$\eta = \bar{Q} \left\{ \tau - a\sqrt{\tau} \exp \left[-\frac{(\tau - c)^2}{b\tau} \right] \right\}. \quad (9.34)$$

The second equation in (9.32), rewritten in explicit form becomes:

$$\frac{dC}{C} = -\frac{[-\text{Ei}(-\eta/\tau)] e^{-\tau}}{-\{1 - \tau e^{-\tau}[1 - (\eta/\tau)\text{Ei}(-\eta/\tau) - e^{-\eta/\tau}]\}} d\eta, \quad (9.35)$$

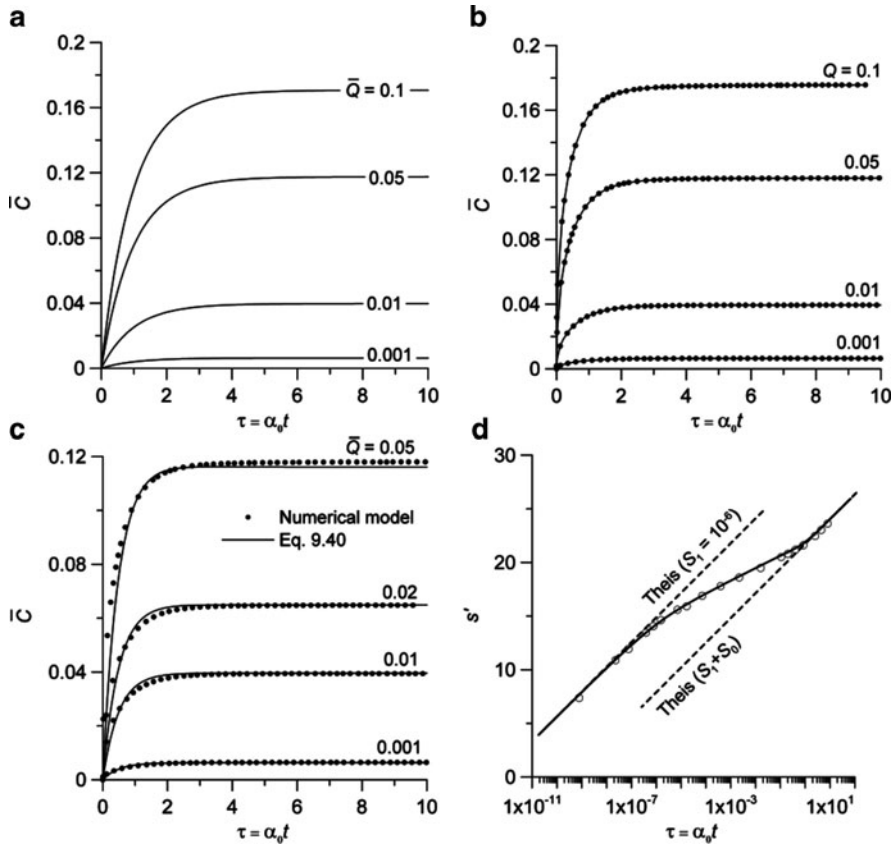


Fig. 9.5 (a), (b), (c) Function $\bar{C}(\tau)$ plotted at different values of dimensionless group $\bar{Q}$. (a) Solution of a system of Eqs. 9.32; (b) numerical solution of fully coupled 2D systems of differential equations for flow and solute transfer in radial coordinates using TOUGH2 simulator; (c) a comparison of approximate analytical solution (Eq. 9.40) with the modeling data. (d) Dimensionless drawdown in the pumping well, $s'_{w,1} = 4\pi T_1 s_{w,1}/Q_w$, vs. dimensionless time, $\tau = \alpha_0 t$ ($\alpha_0 = 2k_0/S_0 m_0$); $S_1/S_0 = 0.001$, $S_0 = 0.001$ (dots correspond to the numerical solution, solid curve corresponds to the analytical solution from Moench 1985, dashed lines are the asymptotic Theis's solution)

or with $d\eta/d\tau = \eta' = \eta'(\tau)$, the derivative of dimensionless coordinate η (9.33), we obtain

$$\frac{dC}{C} = - \frac{[-\text{Ei}(-f(\tau))] \eta' e^{-\tau}}{-\{1 - \tau e^{-\tau} [1 - f(\tau) \text{Ei}(-f(\tau)) - e^{-f(\tau)}]\}} d\tau, \quad (9.36)$$

where function $f(\tau)$ is determined by Eq. 9.33. The integration of the latter equation allows the solution of the problem to be represented in the integral form:

$$\bar{C}(\tau) = 1 - \exp \left(- \int_0^\tau \frac{[-\text{Ei}(-f(\theta))] \eta' e^{-\theta}}{1 - \theta e^{-\theta} [1 - f(\theta) \text{Ei}(-f(\theta)) - e^{-f(\theta)}]} d\theta \right), \quad (9.37)$$

$\bar{C}(\tau) = (C_1 - C_{10}) / (C_{20} - C_{10})$, $\tau = \alpha_0 t$ (t is time). The results obtained from calculations by (9.37) are rather close to the exact solution of the problem, given by system of Eq. 9.32.

Now analysis of plots in Fig. 9.4b shows that, in the practically important ranges of parameter $\bar{Q}$ (< 0.1), the dimensionless ratio

$$\frac{\eta}{\bar{Q}\tau} = \frac{\pi m_1 \phi_1 r^2}{Q t} \quad (9.38)$$

is close to unity. Therefore we can assume that $\xi \approx \bar{Q}$ and $\eta \approx \bar{Q}\tau$; the latter identity implying that water squeezing from the low-permeability layer does not cause any deviation of the calculated flow rate from the values found from the formula for an isolated bed: $q_1 = Q / 2\pi m_1 r$.

Therefore, a simpler approximation can be proposed:

$$\bar{C} = 1 - \exp \left(- \int_0^\tau \frac{\bar{Q} (-\text{Ei}(-\bar{Q})) e^{-\theta}}{1 - \theta e^{-\theta} (1 - Q \text{Ei}(-\bar{Q}) - e^{-\bar{Q}})} d\theta \right). \quad (9.39)$$

Taking into account that the denominator under the integral (9.39) at $\bar{Q} < 0.1$ is close to unity, we obtain

$$\bar{C} = 1 - \exp \left[-\bar{Q} (-\text{Ei}(-\bar{Q})) (1 - \exp(-\tau)) \right]. \quad (9.39a)$$

As it was mentioned in the Sect. 9.1.1, the considered solute transport model formulation is based on a quasi-steady-state assumption, which is not necessarily true for the area of influence of the cone of depression where solutes are transiently squeezed from the semipervious bed. Indeed, numerical modeling shows the appreciable deviation of the numerical benchmark solution from the presented above analytical formulas (Fig. 9.5b). At the same time, we may efficiently use formula (9.39a) to improve the quasi-steady-state model as follows:

$$\bar{C} \approx \left[1 - \exp(\bar{Q} \text{Ei}(-\bar{Q})(1 - \exp(-\tau))) \right] \frac{1 - \exp(-2\tau)}{1 - \exp(-\tau)}. \quad (9.40)$$

As one may see such fitting formula makes analytical results to be in good agreement with the modeling data (Fig. 9.5c). For small values of the dimensionless discharge rate, $\bar{Q} \leq 0.02$,

$$\bar{C} \approx -\bar{Q} \text{Ei}(-\bar{Q}) (1 - \exp(-2\tau)). \quad (9.41)$$

The maximal concentration at $\tau = \alpha_0 t > 1 \div 2$ is

$$\bar{C} = \bar{C}_{\max} \approx 1 - \left(\frac{\bar{Q}}{0.6} \right)^{\bar{Q}} \quad (\bar{Q} < 0.05 \div 0.1). \quad (9.42)$$

Overall, proceeding from the actual values of the flow and transfer properties of aquifers and separating clay beds, the impact on which can be characterized by low values of the dimensionless group $\bar{Q} = Q/4\pi m_1 \phi_1 a^* \approx Q_w S_0/4\pi m_1 \phi_1 T_1$, we find that the anticipated maximal relative concentrations of solutes in the pumped-out water (these solutes originate from clay interstitial solution) are unlikely to exceed 5–10%. This conclusion looks somewhat paradoxical, since the major water volume entering the wells is known (Hantush 1960, 1964) to be due to the elastic reserves in clay beds. This seeming contradiction will dissolve if we mention that the water reserves in an aquifer, which are reduced by dewatering, are forming in the marginal part of the depression cone and, in virtue of the nonmonotonic (impulse-like) behavior of function $q_0(r, t)$ over time, the water-carrying bed receives limited amounts of salts from clays in this zone. The farther migration of solutions takes place in the zone where water reserves in the clay bed have already been depleted, resulting in that salt concentrations in the transit flow does not increase. Since the zone of clay interstitial water input into the producing aquifer steadily shifts from the well, the time required for solutions from this zone to reach the well in the radial flow also steadily increases, thus also facilitating the concentration curve rapidly becoming more level. The corresponding time required for limiting values to be reached satisfies the inequality $t(\bar{C}_{\max}) \approx (0.5 \div 1) S_0 m_0 / k_0$.

9.2 Change in the Water Quality of Unconfined Producing Aquifer Under the Influence of Weathering Sulphide Mineral Products in Vadoze Zone

9.2.1 Governing Factors and the Scale of the Process

Water intakes in shallow aquifers often feature progressively declining water quality because of the more active hydrogeochemical processes taking place in the aeration zone that forms due to lowering of the water table by pumping. The decline in water quality manifests itself in growing water hardness and the concentrations of sulfates, iron, and some trace elements. The major process is the chemical weathering of sulfide minerals, including their oxidation by atmospheric oxygen, reaching their surface because of dewatering of pores (fissures) during drawdown. Before pumping sulfides were submerged and protected against oxidation (Larsen and Postma 1997; Appelo and Postma 2005).

Very illustrative are observational data on water chemistry variations over 30-year period (Fig. 9.6) in a water intake in the Middle Ural Region (Sverdlovsk

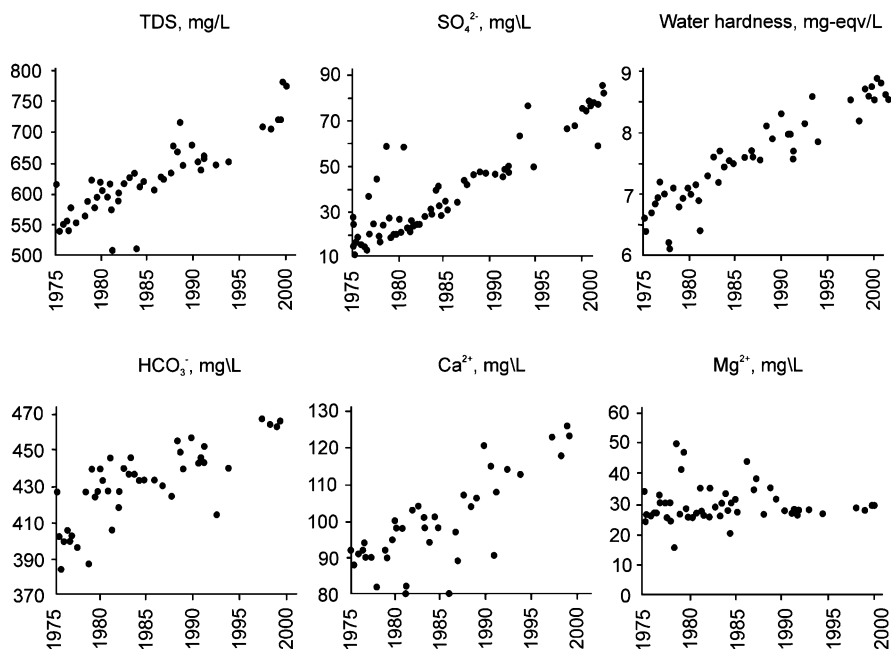


Fig. 9.6 Observational data illustrating water quality changes in wells of Poldnevsky wellfield (Vishnyak 2005; Lekhov and Vishnyak 2005)

province, Russian Federation). Groundwater occurs in a carbonate structure with a limited stretch. Water intake capacity is 18,000–19,000 m³/day. Groundwater drawdown in the center of depression cone reaches 30–35 m. The total area of the zone affected by drainage is about 60 km².

During the operation of the Poldnevskii wellfield, its water chemistry has changed from hydrocarbonate to sulfate-hydrocarbonate; water TDS increased from 0.5 to 0.9 g/l and even more, mostly because of an increase in sulfate-ion concentration from 15 to 60–80 mg/l; and water hardness increased from 6–6.5 to 8–10 mg-equiv/l (Fig. 9.6). Studies (Vishnyak 2005) have shown that the deterioration of groundwater quality in the Poldnevskoe deposit is due to the formation of a pyrite oxidation zone in blanket deposits over the groundwater depression table. Pyrite concentration in these deposits is up to 5 wt. %.

Similar factors govern the formation of anthropogenic pollution plumes in aquifers lying within the zone of influence of overburden dumps in mining areas: sulphide minerals contained in the rock, crushed in the process of mining or during flotation, also undergo oxidation, whose products reach groundwater with infiltrating flow (Mironenko and Rumynin 1999; Elberling et al. 2000; Indraratna et al. 2002; Sracek et al. 2006). To control such pollution, which results, in particular, in large volumes of acid drainage water, is among the most acute environmental problem in mining regions. That is why, sulphide oxidation processes taking place in aerated mine wastes (tailings) are most deeply understood.

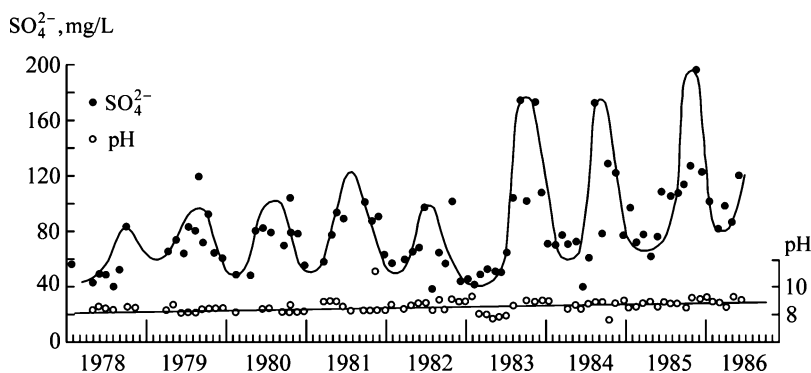


Fig. 9.7 Time variations of the sulfate concentration and pH in the quarry waters of the Kovdorskoe iron-ore deposit

Monitoring data on the Kovdorskoe iron-ore deposit (Kola Peninsula) can be used to illustrate the combined effect of two factors (deep water drawdown and infiltration from mine dump areas) on drainage water quality. A specific hydrochemical type of alkaline groundwater (pH 8.20–8.45) with essentially sulfate calcium composition forms in the western and northern wings of the deposit, and the situation can be regarded as substantial sulfate pollution as the concentration of SO_4^{2-} ions here is almost two orders of magnitude greater than the background level and reach 2–3 MAC (for water bodies used for fishery). Monitoring observations show that SO_4^{2-} ions tend to accumulate in drainage and quarry waters (Fig. 9.7) and pH somewhat increases over time.

The most likely sources of sulfur in groundwater are sulphide minerals, dispersed over the mass of ore-free rocks in mine dumps and within the zone of aerated rocks above the depression surface. Oxidation of sulphides, which are mostly represented by pyrrhotine (its concentration may reach 3%) and pyrite (its concentration varies within 0.1–1.0%), takes place under their active interaction with atmospheric moisture and oxygen.

According to conventional notions, the acidity of the medium would increase. However, hydrochemical materials show the situation to be reversed: pH increases with growing sulfate concentration. If we exclude the effect of microorganisms, such as thionic bacteria, on the course of reactions, the observed hydrochemical transformations can be attributed to the chemical weathering of rocks with alkaline and ultrabasic composition (Mironenko et al. 1998, p. 169). An indirect confirmation that this process is possible is the fact that the newly formed water features a simultaneous increase in the concentration of ions of calcium, a component of rock-forming minerals most typical in the deposit, e.g. diopside (clinopyroxene), anorthite (plagioclase), and some others.

The important contribution of atmospheric recharge to the formation of the hydrogeochemical regime of groundwater (under disturbed conditions) is confirmed by observational data collected in the annual course. Thus, the plot in Fig. 9.7

features distinct sinusoidal pattern (with increasing oscillation amplitude) and a clear tendency toward an increase in SO_4^{2-} during spring and autumn floods, when the interaction between atmospheric moisture and dump rocks becomes more intense. Minimums in SO_4^{2-} concentration are typical of winter low-water period, when the role of such factors is insignificant (Fig. 9.7).

It is common knowledge that the rate of sulfuric acid production is governed by the availability of sulphide surface for oxygen molecules (O_2). The major mechanism of O_2 transport in the partially water-saturated medium is molecular diffusion. O_2 mass flux is controlled by its concentration gradient caused by a decrease in O_2 with depth because of its consumption for sulphide oxidation. The oxidation rate is limited by both reaction kinetics and O_2 diffusion.

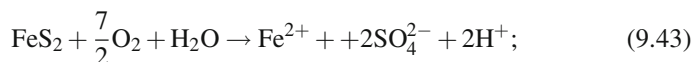
The model discussed below is not meant to reflect all hydrogeochemical processes. It only accounts for O_2 diffusion in the gas phase and the simplest first-order reactions of pyrite oxidation.

9.2.2 Thermodynamics of Chemical Weathering Process

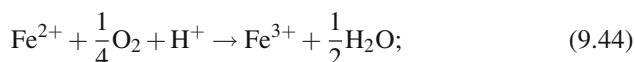
Typical representatives of sulphide minerals scattered in rock formations are pyrite (FeS_2), pyrrhotine (Fe_{1-x}S), chalcopyrite (CuFeS_2), blende (ZnS), and arsenopyrite (FeAsS). Pyrite commonly predominates; therefore, pyrite oxidation reaction is taken as dominating in the model.

The oxidation of pyrite, which is abundant in the Earth's crust, involves several stages, accompanied by the formation of metastable secondary reaction products, such as ferryhydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$), schwertmanite ($\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4 - \text{Fe}_{16}\text{O}_{16}(\text{OH})_{10}(\text{SO}_4)_3$), as well as more stable compounds such as jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), goethite ($\alpha\text{-FeO}(\text{OH})$), and haematite (Fe_2O_3). Pyrite oxidation comprises three major stages (Larsen and Postma 1997; Schippers et al. 1999; Elberling et al. 2000; Bethke 2008):

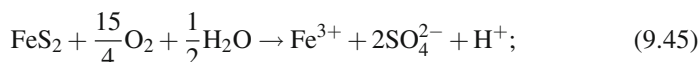
1. pyrite oxidation by oxygen dissolved in film water



2. oxidation of ferrous iron ions into ferric iron

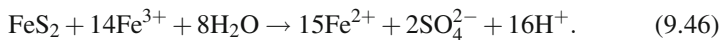


at high pH ($\text{pH} > 4$), this reaction is fast, so Eqs. 9.43 and 9.44 can be combined into



at low pH under abiotic conditions, reaction (9.44) is very slow, however even under such conditions it can be significantly accelerated by microorganisms;

3. pyrite oxidation by ferric iron ions that have formed at the second stage



Although the thermodynamics of reaction (9.45) is not explicitly involved in the model analysis below, its stoichiometric coefficients, ν , are taken into account in determining oxygen consumption during pyrite oxidation and sulphide production (see Sect. 9.2.3).

9.2.3 Sulfide Oxidation Kinetics

Chemical reactions can be characterized, in particular, by their volumetric rate

$$R_{\text{vol}} = \frac{d[M]}{dt} = -\frac{d[M_{\text{Fe}}^{\text{tot}}]}{dt}, \quad (9.47)$$

measured, for example, in static laboratory experiments with crystals of the examined mineral; here $[M]$ is the concentration of the original mineral in solution (mol/l), $[M_{\text{Fe}}^{\text{tot}}]$ is the total concentration of reaction products (Fe ions) in solution (mol/l). The experimental data can be better represented in the form

$$R_{\text{sp}} = R_{\text{vol}} \frac{V}{A}, \quad (9.48)$$

i.e., as the specific oxidation rate, which does not depend on the configuration of the experimental system; here V is the volume of solution, A is the total surface area of minerals. In this case R_{sp} (with dimension of $\text{mol m}^{-2} \text{s}^{-1}$) is defined as the amount of Fe, being released into solution from a unit surface area of sulphide per unit time.

The results of many experiments aimed to study the rate of sulphide oxidation under various conditions are available in the special literature. The range of R_{sp} variations is fairly wide: $R_{\text{sp}} = N \cdot 10^{-9} - N \cdot 10^{-11} \text{ mol m}^{-2} \text{s}^{-1}$.

The most complete notion of sulphide oxidation kinetics in rock can be obtained from the empirical formula:

$$r_c = R_{\text{sp}} S = k' [\text{O}_2(\text{aq})]^m [\text{H}^+]^n, \quad (9.49)$$

where r_c is reaction rate ($\text{mol m}^{-2} \text{s}^{-1}$); $[\text{O}_2(\text{aq})]$ is oxygen activity in the liquid (aq) phase in contact with the active surface of mineral grains; $[\text{H}^+]$ is hydrogen ion activity; m and n are coefficients characterizing the order of reaction, k' is kinetic coefficient (s^{-1}), S is specific surface area of sulphide grains (m^{-1}), which can be approximated as $S = 6G/\rho d$ (G is the weight concentration of sulphide in unit rock material volume, ρ is the density, d is the diameter of grains with isometric shape).

Experiments typically show the oxidation reaction rate to be only slightly dependent on H^+ concentration. Exponent m varies on the average from 1/2 to 1. Several researchers who described this type of reaction assumed $r_c \sim \sqrt{[O_2(aq)]}$ (McKibben and Barnes 1986; Williamson and Rimstidt 1994; Asta et al. 2007; Gandy and Younger 2008). At the same time, linear relationships, i.e., $r_c \sim [O_2(aq)]$ also cannot be ruled out (Elberling and Nicholson 1994; Scharer and Pettit 1994; Lefebvre and Gélinas 1995; Salmon 1999; Blunden and Indraratna 2001; Sracek et al. 2006; Mbonimpa et al. 2003). In the latter option, which appears preferable for conceptual estimates of solute migration in groundwater, the kinetic equation of *first-order* pyrite oxidation reaction in solid (s) phase can be written as (Elberling and Nicholson 1994):

$$r_c = -\frac{d[FeS_2(s)]}{dt} = -\nu \frac{d[O_2(aq)]}{dt} = kC_a, \quad \nu = \frac{4}{15}, \quad (9.50)$$

where ν is a stoichiometric coefficient, which can be determined from reaction (9.45) and shows that the oxidation of 1 mol of pyrite requires 3.75 mol of O_2 , C_a is oxygen concentration in soil air (mol m^{-3}), k is a generalizing coefficient of reaction rate (1/s), accounting, in particular, for the linear relationship between oxygen concentrations in liquid and solid phases. For sulfate ion, as a reaction product, we have

$$r_c = -\frac{d[FeS_2(s)]}{dt} = \nu \frac{d[SO_4^{2-}(aq)]}{dt} = kC_a, \quad \nu = \frac{1}{2} \quad (9.51)$$

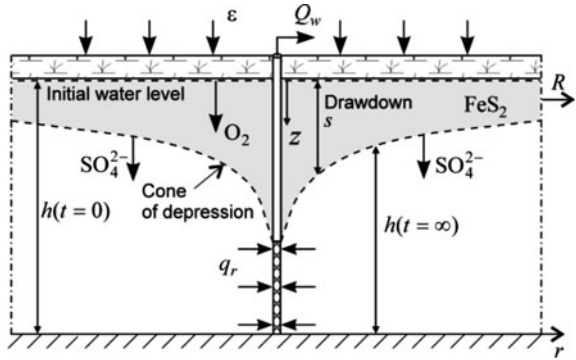
(one mole of FeS_2 produces two moles of SO_4^{2-}). The first-order model of pyrite oxidation does not contradict experimental data (Nicholson et al. 1988, 1990), obtained at low O_2 concentration in gas phase (tentatively, at $C_a < 0.05$ atm). As will be shown below (see Sect. 9.2.5), the right-hand parts of kinetic Eqs. 9.50 and 9.51 can be modified to include the “reversible” component of the chemical reaction.

As mentioned above Fe^{+3} ion is a fairly strong oxidizer (9.46), and at low pH, the rate constant of the corresponding reaction exceeds that in kinetic Eq. 9.50 by almost an order of magnitude (Xu et al. 2000). Since the rate of pyrite oxidation by ferric iron is greater than that by oxygen, the reaction of Fe^{2+} change into Fe^{3+} (9.44) can become the oxidation-limiting process. With the effect of the microbiological factor and the heterogeneity of the system taken into account, and considering the uncertainties of the process, it becomes clear that the linear model is the most suitable for process analysis.

9.2.4 Distribution of Oxygen and Sulfates in the Vadoze Zone

Groundwater level drawdown during water intake allows atmospheric oxygen to reach sulphide minerals scattered in the sediments or rocks, resulting in their oxidation (Fig. 9.8). The products of this reaction enter mobile water phase and move downward with infiltrating water.

Fig. 9.8 A conceptual diagram for sulfate water formation during water pumping out of a well (the grey color marks the pyrite oxidation zone within depression cone)



9.2.4.1 Oxygen Migration

The main mechanism of oxygen transport in the air phase within the vadoze zone from near-surface soil layers to groundwater table is molecular diffusion (Refsgaard et al. 1991; Blunden and Indraratna 2001; Mbonimpa et al. 2003; Sracek et al. 2006). The concentration gradient is maintained by oxygen consumption for sulphide oxidation. The above-given rate of diffusion supply of oxygen to the crystalline surface of sulphide, where chemical reactions take place, is many times greater than the rate of those reactions. This allows the diffusion process to be considered in the steady-state formulation

$$D_a \frac{d^2 C_a}{dz^2} = r_c = k C_a, \quad (9.52)$$

where z is the vertical coordinate directed downwards ($z = 0$ is the upper boundary at $t = 0$, when water intake started, Fig. 9.8); D_a is the effective coefficient of molecular oxygen diffusion in partially water-saturated subsurface material, which can be determined from the expression (Aachib et al. 2004)

$$D_a = \frac{1}{\phi^2} (D_a^0 \theta_a^{p_a} + H D_w^0 \theta_w^{p_w}); \quad (9.53)$$

here D_a^0 , D_w^0 are molecular diffusion coefficients of oxygen in air ($\sim 1.56 \text{ m}^2/\text{day}$) and water ($\sim 2.16 \cdot 10^{-4} \text{ m}^2/\text{day}$), ϕ is porosity, p_a and p_w are empirical coefficients, characterizing the connectivity of pores filled by air and water (it can be assumed that $p_a = p_w \approx 3.3$), θ_a and θ_w are the volumetric air and water content in the rock, H is Henry's equilibrium constant (~ 0.03 for oxygen at 20°C).

Boundary conditions for the problem in question:

$$C_a(z=0) = C_a^0, \quad \frac{dC_a}{dz}(z=s) = 0. \quad (9.54)$$

The first condition reflects the unlimited access of oxygen into the vadoze zone from the surface; C_a^0 can be assumed to be equal to oxygen concentration in the

atmosphere (about 8.17 mol/m^3). The second condition refers to the reflecting boundary (groundwater table, $z = s$) and follows from the assumption that D_a is many times greater than the diffusion coefficient D_w of dissolved gas in the liquid phase (groundwater); $s = s(r)$ is the groundwater level drawdown.

The general solution of (9.52) has the form (Carslaw and Jaeger 1959; Kamke 1977)

$$C_a = C_1 e^{-z\sqrt{a}} + C_2 e^{z\sqrt{a}}, \quad (9.55)$$

$a = k/D_a$, C_1, C_2 are integration constants, which can be found from boundary conditions (9.54). Finally we have:

$$C_a = C_a^0 \frac{e^{-(s-z)\sqrt{a}} + e^{(s-z)\sqrt{a}}}{e^{-s\sqrt{a}} + e^{s\sqrt{a}}} = C_a^0 \frac{\text{ch}[(s-z)\sqrt{a}]}{\text{ch}(s\sqrt{a})}. \quad (9.56)$$

The latter expression allows us to elucidate the variation law (an increase over time) of the concentrations of other components, in particular, sulfates, in pore water (liquid phase). It is this component, which is among indices of this type of groundwater pollution, that will be considered below as the main marker of the process in question.

9.2.4.2 Migration of Sulfates

The advective transport of SO_4^{2-} ions (with current concentration of C') in the vadoze zone can be described by the equation:

$$\theta \frac{\partial C'}{\partial t} + \varepsilon \frac{\partial C'}{\partial z} + \frac{\theta}{v} \frac{\partial [\text{FeS}_2(s)]}{\partial t} = 0, \quad (9.57)$$

where the last term in the left part of the equation reflects the rate of sulphide oxidation in solid phase (s) in the kinetic reaction (9.51); here ε is infiltration rate (a constant), θ is the mean moisture content. Now, since concentration C_a in (9.51) is determined by (9.56), balance Eq. 9.57 can be represented in the following dimensionless form:

$$\frac{\partial \bar{C}'}{\partial \tau} + \frac{\partial \bar{C}'}{\partial \xi} = \frac{\text{ch}[\beta(\bar{s} - \xi)]}{\text{ch}(\beta \bar{s})}, \quad (9.58)$$

where

$$\bar{C}' = C' \varepsilon v / (C_a^0 k m \phi), \quad \tau = \varepsilon t / m \phi, \quad \xi = z \theta / m \phi, \quad \bar{s} = s \theta / m \phi, \quad \beta = \sqrt{a} m \phi / \theta. \quad (9.58a)$$

Let us substitute free variables (Golubev 1981, p. 58):

$$\tau_1 = \tau - \xi, \quad \xi_1 = \xi, \quad (9.59)$$

i.e., the time in point ξ is measured since the moment $\tau_0 = \xi$ when infiltration water reaches this point. From the rules of differentiation of composite functions, we have

$$\frac{\partial \bar{C}'}{\partial \xi} = \frac{\partial \bar{C}'}{\partial \xi_1} \frac{\partial \xi_1}{\partial \xi} + \frac{\partial \bar{C}'}{\partial \tau_1} \frac{\partial \tau_1}{\partial \xi} = \frac{\partial \bar{C}'}{\partial \xi_1} - \frac{\partial \bar{C}'}{\partial \tau_1}, \quad (9.59a)$$

$$\frac{\partial \bar{C}'}{\partial \tau} = \frac{\partial \bar{C}'}{\partial \tau_1} \frac{\partial \tau_1}{\partial \tau} + \frac{\partial \bar{C}'}{\partial \xi_1} \frac{\partial \xi_1}{\partial \tau} = \frac{\partial \bar{C}'}{\partial \tau_1}. \quad (9.59b)$$

Now, from (9.58) we obtain

$$\frac{\partial \bar{C}'}{\partial \xi_1} = \frac{\text{ch}[\beta(\bar{s} - \xi_1)]}{\text{ch}(\beta \bar{s})}. \quad (9.60)$$

Separating variables and integrating this expression with respect to concentration from 0 (sulfate concentration at the upper boundary of the oxidation zone $\xi_1 = 0$) to $\bar{C}'$ (the current value) and with respect to the dimensionless space coordinate from 0 to ξ_1 , we obtain

$$\bar{C}' = \frac{\text{sh}(\beta \bar{s}) - \text{sh}[\beta(\bar{s} - \xi_1)]}{\beta \text{ch}(\beta \bar{s})}, \quad \tau_1 > 0 \quad (\tau > \xi). \quad (9.61)$$

At $\xi_1 = \bar{s} = \tau$, we obtain the expression, describing variations of sulfate concentration in infiltration water at the depression surface:

$$\bar{C}'(\xi_1 \rightarrow \bar{s}) \equiv \bar{C}^*(\tau, \bar{s}) = \frac{\text{sh}(\beta \tau)}{\beta \text{ch}(\beta \bar{s})}. \quad (9.62)$$

At $\beta \rightarrow 0$ (the case when moisture motion in the vadoze zone has only slight effect on the concentration distribution)

$$\bar{C}^*(\tau, s) = \frac{\tau}{\text{ch}(\sqrt{a}s)}. \quad (9.63)$$

The latter equality can also be obtained by integrating (9.51) at concentration C_a , determined from Eq. 9.56. The latter equality shows, in particular, that sulfate concentration in this case increases linearly over time.

9.2.5 Sulfate Migration in an Aquifer

Sulfate mass balance equation for a radial flow, analogous to Eq. 9.1, has the form

$$m\phi \frac{\partial C}{\partial t} + m \frac{1}{r} \frac{\partial}{\partial r} r [q(r)C] - \varepsilon C^*(r, t) = 0, \quad (9.64)$$

where $C = C(r, t)$ is the current concentration of sulfates in the aquifer; $C^*(r, t)$ is current sulfate concentration at the depression surface; m and ϕ are the mean thickness of the aquifer and the active porosity of aquifer material, respectively; ε is the infiltration recharge.

Further transformations (see Sect. 9.1.1) yield the following partial differential equation:

$$\frac{\partial C}{\partial t} + u_r \frac{\partial C}{\partial r} + \varepsilon^* [C - C^*(r, t)] = 0, \quad (9.65)$$

where $u_r = q_r / \phi$ is the actual (radial) flow velocity, $\varepsilon^* = \varepsilon / m\phi$.

Let us describe the groundwater level drawdown in the aquifer by the approximate equation

$$s = s(r) \approx \frac{Q_w}{4\pi T} \ln \left(\frac{R}{r} \right)^2, \quad (9.66)$$

i.e., Dupuit formula for steady-state radial flow; here R is the range of influence, determined from the simple balance equation $\pi R^2 \varepsilon = Q_w$; T is the mean transmissivity. Now $u_r = Q_w / 2\pi r m\phi$.

9.2.5.1 General Solution

Equation 9.65 for the input concentration function at the depression surface, determined from (9.62), can be transformed into the following dimensionless form:

$$\frac{\partial \bar{C}}{\partial \tau} + \frac{\partial \bar{C}}{\partial \eta} + \left(\bar{C} - \frac{\text{sh}(\beta \tau)}{\beta \text{ch}[\alpha \ln(\eta)]} \right) = 0, \quad (9.67)$$

where

$$\bar{C} = \frac{\varepsilon v C}{C_a^0 k m \phi}, \quad \eta = \frac{r^2}{R^2}, \quad \tau = \frac{\varepsilon t}{m\phi}, \quad \alpha = \frac{Q_w}{4\pi T} \sqrt{\frac{k}{D_a}}, \quad \beta = \frac{m\phi}{\theta} \sqrt{\frac{k}{D_a}}. \quad (9.67a)$$

The partial differential equation corresponds to the system of ordinary differential equations

$$\frac{d\tau}{1} = \frac{d\eta}{1} = - \frac{d\bar{C}}{\bar{C} - \frac{\text{sh}(\beta \tau)}{\beta \text{ch}[\alpha \ln(\eta)]}}. \quad (9.68)$$

Since we focus on sulfate concentration in the withdrawal well, we have $\eta = \tau$. In this case, instead of system of Eqs. 9.68, we obtain the single differential equation

$$\frac{d\bar{C}}{d\tau} + \bar{C} = \frac{\text{sh}(\beta \tau)}{\beta \text{ch}[\alpha \ln(\tau)]}. \quad (9.69)$$

By substituting $\bar{C} = ye^{-\tau}$, we obtain an ordinary differential equation with separating variables, whose solution yields:

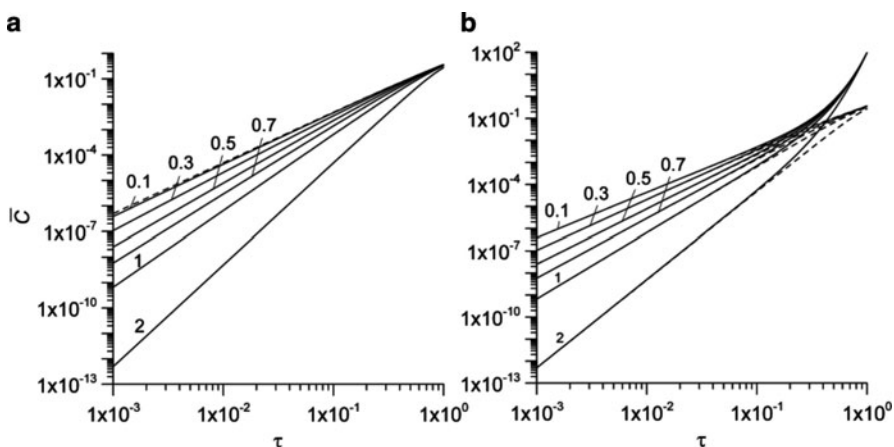


Fig. 9.9 Function $\bar{C}(\tau)$ at different values of group α (figures at the curves): (a) $\beta = 0$ (dashed line is approximate solution (9.71)), (b) $\beta = 10$ (dashed lines are for $\beta = 0$)

$$\bar{C} = e^{-\tau} \int_0^{\tau} e^x \frac{\text{sh}(\beta x) dx}{\beta \text{ch}[\alpha \ln(x)]}. \quad (9.70)$$

Analysis of plots of this solution (Fig. 9.9) shows, in particular, that with fixed k , D_a and ϵ , the values of sulfate concentrations in the pumped-out water are determined by the ratio Q/T : an increase in this ratio (an increase in dimensionless group α) reduces the calculated concentration values. Indeed, the greater is Q/T , the deeper lies the depression curve from the surface and the less available is oxygen for the lower (near the depression surface) zone of aerated sediments or rocks. The result is a lower rate of oxidation and hence a lower rate of sulfate production. The process of groundwater quality formation is sensitive to variations of β , which, along with ϵ , is responsible for the rate of advection in the aeration zone, only at the later stages of water intake.

Moreover, at $\alpha < 0.1$ and $\beta < 1$, which corresponds to a wide range of conditions, the process is only slightly sensitive to the absolute values of these parameters. This also follows from the asymptotic behavior of solution (9.70), which can be asymptotically represented as

$$\bar{C} \approx e^{-\tau} + \tau - 1, \quad (9.71)$$

where at $\tau < 0.1$, we have $\bar{C} \approx \tau^2/2$. From here it follows that function C grows as the water intake operation time squared: $C \approx C_a^0 k \epsilon^* t^2$, where $\epsilon^* = \epsilon/m\phi$ is a characteristic of water exchange rate in the aquifer, which can be evaluated, for example, by isotopic techniques; $C_a^0 \approx 8.17 \text{ mol/m}^3$. Thus, at $k = 10^{-3} \text{ d}^{-1}$, $\epsilon^* = 2 \cdot 10^{-5} \text{ d}^{-1}$, $C_{\text{SO}_4^{2-}} \approx 1.6 \cdot 10^{-5} t^2 \text{ mg/l}$ (time t is measured in days).

The obtained solution (9.70) is subject to limitations associated with (i) the initial assumption that the reserves of sulphides in the aeration zone are unlimited;

(ii) the simplified form of kinematic equations, neglecting the possible formation of inhibiting films on the surface of minerals that undergo oxidation (Nicholson et al. 1990; Lekhov and Vishnyak 2005), the result of those films being a significant decrease in the rate of the process; and (iii) the neglect of the chemical reaction that may involve sulfates, for example, gypsum formation. Therefore, the proposed model will, most likely, yield too conservative forecast estimates (in terms of the anticipated extent of water quality changes in the water intake).

In the light of these facts, the development of models should be aimed to reflect, in the initial problem formulation, the additional features of pyrite oxidation in the vadoze zone.

9.2.5.2 The Formation of Sulphide Leaching Front

Let the initial reserves of pyrite in the subsurface material are limited and can be characterized by the concentration of N_0 (mol/m³), and the current concentration is $N = N(t) (\equiv [\text{FeS}_2(s)])$. Now, integrating (9.50), we obtain the linear relationship

$$N(t) = N_0 - kC_a t = N_0 - kC_a^0 \frac{\text{ch}[(s-z)\sqrt{a}]}{\text{ch}(s\sqrt{a})} t, \quad (9.72)$$

which suggests that after a time period of

$$t_0 = \frac{N_0}{kC_a^0} \left(\tau_0 = \frac{\varepsilon N_0}{\text{km}\phi C_a^0} \right), \quad (9.73)$$

a zone of complete pyrite leaching will start forming near section $z = 0$. To determine the rate of its displacement at $t > t_0$, let us write the balance equation

$$N_0 dz = D_a \left. \frac{dC_a}{dz} \right|_{z \rightarrow 0} dt. \quad (9.73a)$$

This equation implies that the mass of FeS_2 released from the rock as the boundary displaces by dz is determined by the diffusion flux through this boundary within time dt . From here (at $z \ll s$), we obtain the velocity

$$\frac{dz}{dt} \approx \frac{C_a^0 \sqrt{kD_a}}{N_0}. \quad (9.74)$$

Expression (9.74) was obtained before for geochemical systems with molecular diffusion dominating in the pore space (Golubev 1981, p. 57). At the moving boundary, we have $C_a = C_a^0$. Clearly with this boundary approaching the groundwater table, the oxidation processes near the water surface become more active, thus accelerating the production of sulfates. During this process, pyrite reserves available for oxidation rapidly become exhausted near the periphery of the depression cone,

after which the aquifer will receive infiltration water with the original quality. To solve the problem in this formulation, let us identify several stages of the process.

At the initial stage, while the completely leached zone has not formed ($t < t_0$, or, in the dimensionless form, $\tau < \tau_0$), solution (9.70) works.

Later ($t > t_0$ or $\tau > \tau_0$), the motion of the leached-zone front can be associated with a decrease in the drawdown

$$s = s_0 - \frac{C_a^0 \sqrt{kD_a}}{N_0} (t - t_0), \quad (9.75)$$

where $s_0 = s_0(r)$ is the function (9.66), describing the actual position of the depression surface. In dimensionless form:

$$\sqrt{as} = \sqrt{as_0} - \gamma(\tau - \tau_0), \quad \gamma = \frac{C_a^0 km\phi}{N_0 \varepsilon} = \frac{1}{\tau_0}, \quad \tau = \frac{\varepsilon t}{m\phi}, \quad \tau_0 = \frac{\varepsilon t_0}{m\phi}. \quad (9.76)$$

Now the solution of the problem becomes

$$\bar{C} = e^{-\tau} \int_0^{\tau} e^x \frac{x dx}{\text{ch}[\alpha \ln(1/x) - \gamma(\tau - \tau_0)]}, \quad \tau > \tau_0, \quad (9.77)$$

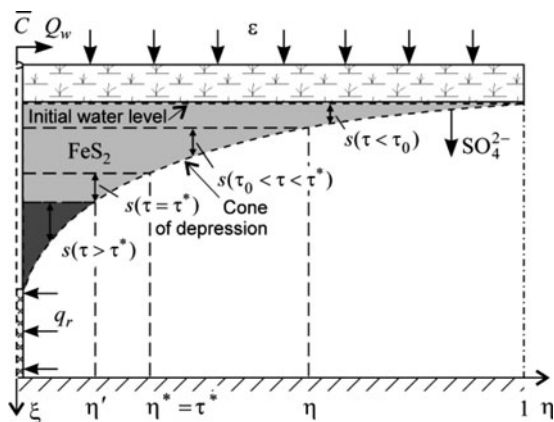
implying successive changes of the stationary states of the effective function $s(r)$. Here we assume $\beta = 0$ to simplify the subsequent analysis.

At the moment $\tau = \tau^*$, determined by the transcendent formula

$$\tau^* = \tau_0 [1 - \alpha \ln(\tau^*)], \quad (9.78)$$

the boundary of the particle capture zone in the aquifer ($\eta^* = \tau^*$) comes in contact with the moving boundary of the depression surface domain (Fig. 9.10), within which clear infiltration water enters the system (that is, when $\eta > \eta^*$, we have $\bar{C} = 0$,

Fig. 9.10 A Schematic diagram for conceptual model of water quality formation under condition of pyrite leaching in the vadoze zone. The domain colored light grey contains the original pyrite distribution, the dark grey domain shows pyrite in the vadoze zone during long water withdrawal periods ($\tau > \tau^*$)



i.e., sulphide reserves are exhausted and sulfate concentration in infiltration water is zero). Expression (9.78) follows from the evident equality

$$\frac{C_a^0 \sqrt{kDa}}{N_0} (t^* - t_0) = \frac{Q_w}{4\pi T} \ln \left(\frac{R}{r} \right)^2 \bigg|_{r=r^*}. \quad (9.78a)$$

Therefore, when $\tau > \tau^*$, the behavior of the concentration function $\bar{C}(t)$ demonstrates the effect of dilution of solutions entering the well by clear infiltration water.

The input of sulfates into the aquifer within the zone limited at $\tau > \tau^*$ by a moving boundary with the coordinate

$$\eta' = \left(\frac{r}{R} \right)^2 = \exp \left[-\frac{\gamma}{\alpha} (\tau - \tau_0) \right], \quad (9.79)$$

is controlled by the effective length of oxygen migration in the vadoze zone, which is also determined by (9.76). The identity of relationships (9.76) and (9.79) allows one to use solution (9.77) to describe all time boundaries of the process (when $\tau > \tau_0$).

Plots in Fig. 9.11 reflect the main features of sulfate migration as pyrite oxidation products throughout the process stages. It can be clearly seen that the low concentrations of pyrite in the vadoze zone (high values of parameter γ) increase the degree of groundwater saturation with sulfates at the initial stages of the process. This is due to the active penetration of oxygen into deeper horizons (due to the higher velocity of the front of the leaching zone in aerated sediments or rocks), maintaining the intense production of sulfuric acid near the depression surface. However, the depletion of sulphide reserves becomes more rapid, resulting in a more considerable drop in sulfate concentration in water at later water withdrawal stages as compared with the

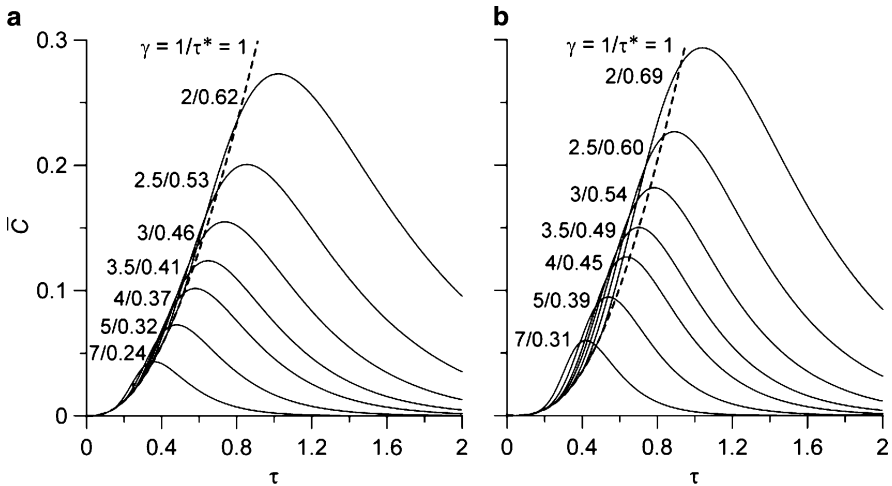


Fig. 9.11 Function $\bar{C}(\tau)$ at limited FeS_2 reserves in the vadoze zone. Figures at curves are γ/τ^* ratios, the dashed line is for $\gamma \rightarrow \infty$ ($N_0 = 0$), $\beta = 0$. (a) $\alpha = 0.5$, (b) $\alpha = 1$

case of higher pyrite saturation of covering deposits (low γ values). Moreover, the comparison of the left and right plots (Fig. 9.11) shows that the increase in α , which can be associated with an increase in the occurrence depth of groundwater surface ($\alpha \sim S \sim Q_w/4\pi T$), results in an increase in the amount of sulfates, which enter the well during the water withdrawal period. This regularity is in agreement with the physical notions, according to which the reserves of pyrite available for oxidation, are proportional to s .

Overall, the extreme character of curves $C(t)$ (Fig. 9.11) can be attributed to the gradual decrease in the size $r(t)$ of the input zone of sulfate-polluted infiltration water $C(t) \sim \varepsilon r^2(t)C_a^0/Q_w$ (see Eq. 9.79) (Fig. 9.10).

In whole, the results of this analytical model study show that lowering the water table in a well field may cause serious problems with sulfate and trace elements in groundwater due to pyrite oxidation.

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Part IV

Lumped-Parameter Models for Flow and Solute Balance in Coupled Surface-Water/Groundwater Systems

The previous chapters have focused on physically based, distributed-parameter models that are based on rigorous mathematical formulations of physical laws governing the flow and solute transport in the subsurface. In addition to such models, flow and migration models with generalized hydrogeological parameters can be used to describe several parallel processes in areas with distinct catchments. These *catchment-scale models* are often called the *lumped-parameter models* or *reservoir models*. The lumped-parameter approach has been widely used in the analysis of stream flow discharge in response to some precipitation event over a watershed (Gelhar and Wilson 1974; Duffy and Gelhar 1985; Maloszewski and Zuber 1993; Pozdniakov and Shestakov 1998; Zuber and Cieczkowski 2000; Maloszewski et al. 2000; Uhlenbrook et al. 2000; Shestakov and Pozdniakov 2003). Although most of these models use empirically-based lumped-parameter formulations, neglecting or oversimplifying the underlying physical processes, they serve their purpose and provide basic data without going through a detailed analysis. Lumped-parameter models can be simply validated with the available hydrological data and global tracer concentration measurements (Maloszewski et al. 2000). Moreover, some experts state that sometimes simpler reservoir, less data-intensive models provide as good or better prediction than physically-based models.

The development of lumped-parameter models described in the first chapter of this section involves (1) their subsequent use for isolating deep percolation (groundwater recharge) as a separate component of total water balance of catchments (Carter et al. 2002; Tsutsumi et al. 2002; Farmer et al. 2003), and (2) the construction of analytical solutions for concentration response functions recorded in the discharge zone of runoff and groundwater flows.

The concluding chapter of this part is devoted to the analysis of the interaction conditions between surface and subsurface waters, governing the water-and-salt balance of the basin in which evaporation sedimentation of salts takes place.

Chapter 10

Conceptual Lumped-Parameter Models for Coupled Transient Flow and Solute Transport in Catchments

The major objective of this chapter is to determine the effect of runoff–infiltration partitioning on hydrochemical or isotopic response of a catchment (Fig. 10.1) under conditions of variable rainfall rate and transient flow process. The lumped-parameter formulation of the flow problem significantly simplifies the search of solute transport problem that makes practically possible the long-range prediction of chemical component distributions between the near-surface domain and the aquifer system relying on a restricted number of hydrogeological parameters.

10.1 Basic Concepts and Definitions

The considered flow models address the partitioning of stream flow contributions from near-surface runoff and from groundwater that manifests itself in quick and slow components of the stream hydrographic record (Fig. 10.2). In this plot one may distinguish *quickflow*, the direct response to a rainfall event, including overland flow and lateral movement in the soil profile, and *baseflow*, the longer-term discharge derived from natural storages, mostly assumed to be groundwater discharge from a shallow unconfined aquifer. Thus, determination of the base-flow and near-surface flow components of stream flow is necessary to understand the hydrologic budgets of surface-water and groundwater basins. Base-flow separation can also provide a groundwater flow measurement for calibration of numerical models (Yu and Schwartz 1999; Huyck et al. 2005).

In addition to the flow models with lumped parameters, coupled solute catchment-scale transport models are also developed to simulate the migration of chemical substance between surface and subsurface domains. It will be shown that the chemical approach involving isotope data analysis is also a way to increase the reliability of hydrograph separation with the aim to study water budget and surface/subsurface contaminant transport potential of the catchments.

For example, the effect of the *quick* and *base* components of surface and subsurface runoff on the character of hydrochemical (concentration) response of the hydrogeological system is illustrated by the study of Kirchner et al. (2000). They have shown a poor time correlation to exist between the flow maximums and

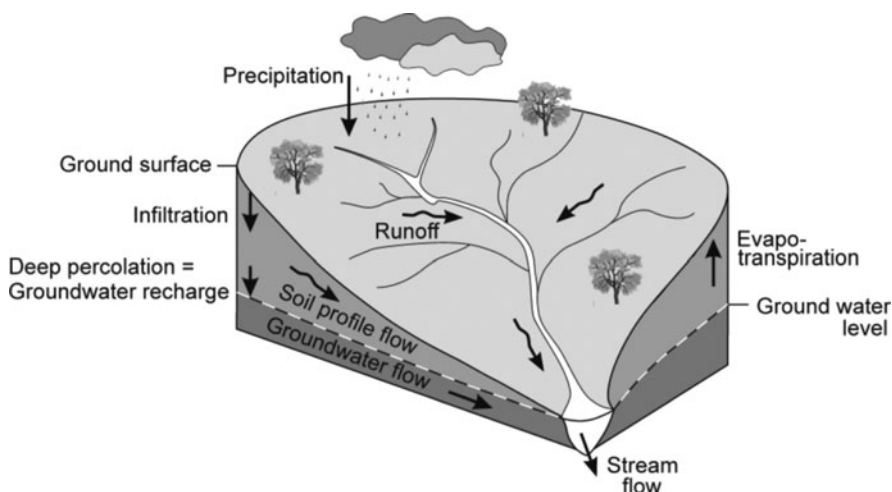
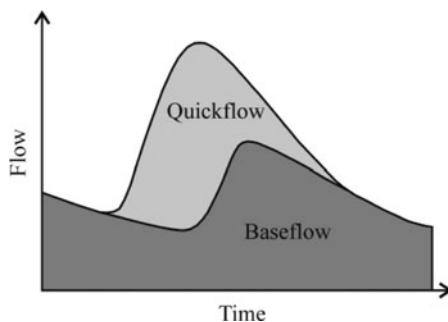


Fig. 10.1 3D conceptual diagram depicting the principal soil-water flow components in a catchment area

Fig. 10.2 The major two flow components of a typical stream hydrograph



minimums in river hydrographs and the appropriate extremums on concentration plots. River water chemistry during maximal rainfall differ from atmospheric water chemistry in the same period and better correlates with the concentrations of components or isotopic tags in the precipitation of previous periods. This demonstrates considerable inertia of the hydrogeological system in hand.

The use of lumped-parameter models does not imply the complication of calculation schemes and the involvement of a large number of parameters (Carter et al. 2002; Tsutsumi et al. 2002). Therefore, their application is justified when the hydraulic and migration parameters are poorly known or when direct methods, such as studying groundwater level variations in aquifers cannot be used because of the poor development of well monitoring system. The construction of models of this type should be based on the comprehensive conceptual understanding of the physics of processes under study. Therefore, we do not identify such models with those based on the black-box principle.

The reliability of results derived from lumped-parameter models increases when there are sufficiently long time series of input and output functions, such as precipitation rates, river water flows, and the concentrations in infiltration and river waters of isotopes or individual chemical components (e.g., chlorides, whose variations are especially significant in coastal regions). Long time series are required to allow one to analyze them with the aim to study the behavior (response) of the system within a wide range of variations in external impacts, since the processes under study can be essentially nonlinear, hampering the linear extrapolation over forecasted conditions.

An advantageous combination of hydrodynamic and hydrochemical components in the construction of coupled models allows one, on the one hand, to use long observational series to obtain physical characteristics of the hydrogeological system and, on the other hand, to predict the effect of existing or potential pollution sources situated in the catchments under study.

In the analysis below, the catchment area (Fig. 10.1) of near-surface water and groundwater contribution is treated as known. For definiteness, we assume that *liquid* precipitation (rain), described by function P , is the major source of moisture within the catchment. In the general case, the function P is essentially nonstationary function $P = P(t)$; it has a random character, and the appropriate time fluctuations feature distinct seasonal trends. The random time function $P(t)$ has a considerable variation and very weak autocorrelation. It is the nonstationarity of function P that determines many features of moisture *partitioning* between the soil and unsaturated geological media) and water layer on the soil surface, responsible for *surface runoff* formation. Therefore, data on the volume of precipitation, averaged over 10 day periods, months, and, all the more, year are of little interest for the subsequent analysis. A sufficiently informative measurement frequency of precipitation depth is 1 day^{-1} , which commonly corresponds to the requirements to standard hydrometeorological observations.

A certain percentage of the rainfall will leave the catchment via mechanisms other than streamflow. These losses are primary evapotranspiration to the atmosphere, groundwater seepage into deep aquifers and water intake due to human activities. We do not claim to give an exhaustive description of precipitation transformation and accumulation processes, which have some specific features in different climatic zones and under different landscape conditions. Such investigations are the focus of many fundamental studies. Our aim (much more modest) is to illustrate the potentialities of some lumped-parameter models, describing the partitioning of atmospheric water in order to obtain flow characteristics (Fig. 10.1), needed to construct transport models.

In this work, two concepts were used for describing near-surface flow contribution to stream flow. The first is based on the assumption that the quick component of near-surface flow is associated with the lateral subsurface flow occurring in the topsoil profile (subsurface runoff). The second concept is based on the assumption that the near-surface contribution includes only surface overflow (actual runoff).

10.2 A Two-Layer Model with Lumped Parameters for Lateral Subsurface Flow and Base Flow

In some catchments with well-developed soil cover, lateral flow in the soil profile (interflow or throughflow) can be the only process of water transmission providing the *quick response* of stream discharge to rainfall. The *delayed response* of stream discharge is produced by the base flow, a process sufficient to maintain stream flow through the year (Weyman 1970). For the hydraulic system under consideration (Fig. 10.3a), the permeable soil layer lies above a semipervious confining layer which separates the soil from underlying aquifer where base unconfined flow occurs. The water generated by precipitation moves downhill and discharges into the surface stream.

The water supply to the upper phreatic aquifer is formed mostly in periods of heavy rainstorms. As it is located bellow the root zone, the recharge rate for the upper temporally functioning aquifer is the difference between the precipitation and the water losses by deep percolation under the root zone. Leakage through the separating layer is the actual groundwater recharge for the lower aquifer where the base flow is formed.

Suppose that water motion in the two-layer system (Fig. 10.3b) takes place within a limited catchment, which can be divided into characteristic streamtubes (Fig. 10.4). The flow that forms due to infiltration recharges into surface stream through those streamtubes. It is assumed that each streamtube represents a specific soil type/vegetative cover combination.

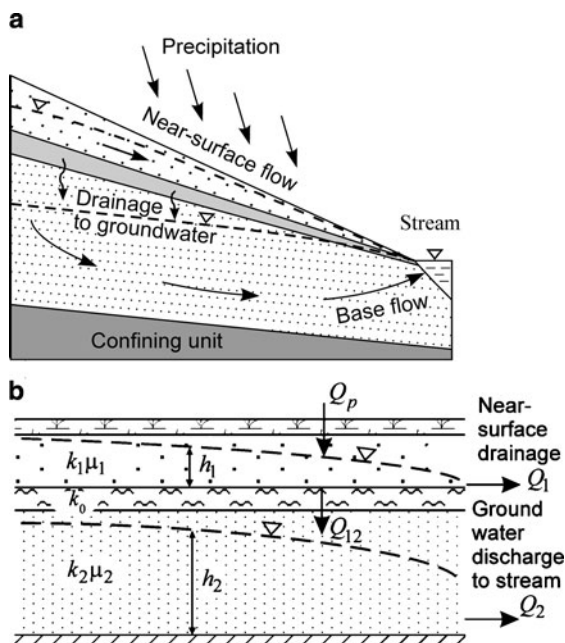
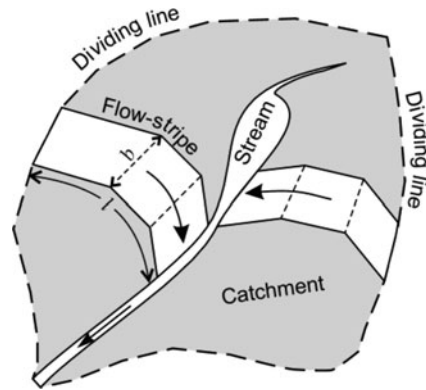


Fig. 10.3 (a) A schematic hydrogeological cross-section of the catchment area, and (b) the relevant conceptualized presentation of the two-layer model

Fig. 10.4 Schematic representation of a river's catchment area and characteristic flow-stripe (streamtubes)



The system of balance equations can be written in the following differential form:

$$\begin{aligned} S_{y1}F \frac{dh_1}{dt} &= Q_p - Q_1 - Q_{12}, \\ S_{y2}F \frac{dh_2}{dt} &= Q_{12} - Q_2, \end{aligned} \quad (10.1)$$

where indices 1 and 2 indicate the upper and lower layers where near-surface and aquifer fluxes are formed; Q_p is the volumetric recharge rate for the upper temporal aquifer within the selected streamtube; $Q_i = Q_i(t)$ is the volumetric discharge rate [L^3T^{-1}]; $Q_{12} = Q_{12}(t)$ is the volumetric vertical drainage rate, in this context corresponding to the groundwater recharge [L^3T^{-1}]; $h_i = h_i(t)$ is the average height of the phreatic surface above the semi-permeable layer or the lower impermeable confining unit as depicted in Fig. 10.3 [L]; S_{yi} is the specific yield [L^3L^{-3}]; F is the area of the arbitrary streamtube [L^2].

Hereafter we assume that the change in water discharge rate dQ_i caused by a precipitation event is related to the increase in the potential function dh_i by

$$dQ_i = \left(\frac{T_i b}{l_e} \right) dh_i, \quad (10.2)$$

where T_i is the transmissivity of the i th layer [L^2T^{-1}]; b is the mean width of flow discharging into the river within a streamtube [L]; l_e is the effective length [L]. As a first approximation, we assume $l_e \approx l/3$ (l is the mean distance between the river and water divide), as is true for the case of steady-state flow in a system where the mean head $h_i \approx h_{0i} + \epsilon l^2/3T_i$ ($T_i = k_i h_{0i}$, h_{0i} is the head at the contour of water discharge) (Gelhar and Wilson 1974).

Substituting dh_i from Eq. 10.2 into the system of Eq. 10.1 yields the system of equations

$$\begin{aligned} \frac{dQ_1}{dt} &= E_1(Q_p - Q_1 - Q_{12}), \\ \frac{dQ_2}{dt} &= E_2(Q_{12} - Q_2), \end{aligned} \quad (10.3)$$

involving only flow components of the basin's water balance. This is a *lumped-parameter* (zero-dimensional) *model*, or simply a *reservoir-type* with generalized kinematic parameters, E_1 and E_2 [T^{-1}]: $E_1 \approx 3T_1/S_{y1}l^2$ and $E_2 \approx 3T_2/S_{y2}l^2$.

The vertical drainage rate (the leakage through the semipervious bed from the upper to the lower layer) is controlled by a relationship between the recharge rate, ϵ , for the upper aquifer and the hydraulic conductivity of the separating bed, k_0 , and depends on the degree of filling with water of the upper layer

$$Q_{12} = \begin{cases} k_0 F \left(1 + \frac{h_1}{m_0} \right) = Q_0 + B_1 Q_1 & \text{for } Q_p > Q_0, \\ Q_p & \text{for } Q_p \leq Q_0, \quad Q_1 = 0, \end{cases} \quad (10.4)$$

$Q_0 = k_0 F$, $Q_p = \epsilon F$ is the volumetric flow of infiltration water, $B_1 = k_0 l^2 / 3T_1 m_0$ is a leakage factor. Obviously, the first equation in (10.4) works when there is water in the upper layer, while the second equation works when it is completely drained, i.e., when the rate of supply is less than the capacity of the separating bed to conduct water ($Q_1 = 0$ is an additional requirement of zero initial condition).

By analogy with previous sections, we will further use specific discharge characteristics $\epsilon_i = Q_i / F$. Now the governing system of Eqs. 10.3 and 10.4 becomes

$$\begin{aligned} \frac{d\epsilon_1}{dt} &= E_1(\epsilon - \epsilon_1 - \epsilon_{12}), \\ \frac{d\epsilon_2}{dt} &= E_2(\epsilon_{12} - \epsilon_2), \end{aligned} \quad (10.5)$$

where

$$\epsilon_{12} = \begin{cases} \epsilon_0 + B_1 \epsilon_1 & \text{for } \epsilon > \epsilon_0, \\ \epsilon & \text{for } \epsilon \leq \epsilon_0; \end{cases} \quad (10.6)$$

the parameter $\epsilon_0 = k_0$ is associated with the carrying capacity of the semipervious bed. As it is seen, the assumption of time-invariant flow properties enables the considered model to be represented in terms of a few lumped parameters (namely, E_1 , E_2 , and B_1), which are the ratios of the layered system characteristics and scale.

The formulation of the problem (10.5–10.6) is of practical significance in the analysis of observational data on the discharge into the river basin of flows that form in the case of an input function with essentially *nonstationary* (time-variable) character, identified with infiltration recharge of the water-bearing strata. Thus, during intense precipitation ($\epsilon > k_0$), “temporal” aquifers form in the upper part of the section, where they serve as a medium for rapid water (moisture) transport from water divide to discharge areas (river valley). In relatively dry periods ($\epsilon \leq k_0$), all precipitation passes into the lower aquifer and only after that discharges into the river. Since the deeper parts of the section have low kinetic constants (E_2), the water that enters the system during relatively dry phases reaches the river with a

considerable time lag. The intense precipitation, enhancing flows in the upper part of the section, rapidly (since commonly $E_1 \gg E_2$) reach the discharge zones and form peak discharges in the river.

Thus, the mechanisms considered above ensure a kind of partitioning of precipitation flow. Such partitioning accounts for the observed *nonlinearity* of river runoff formation process: the mean monthly precipitation being the same, the response of the river can be different, depending on its distribution within the month. To assess the duration of the activity of the upper aquifer under unsteady infiltration, the solution of the problem requires the analysis of water balance in the system.

10.3 Basic Analytical Functions

10.3.1 Steady-State Flow

With $E_1, E_2 \rightarrow \infty$ the solution of Eqs. 10.5 and 10.6 have a trivial form (step-wise input function):

$$\begin{aligned} \varepsilon_1 &= \frac{\varepsilon - \varepsilon_0}{1 + B_1}, \quad \varepsilon_2 = \frac{\varepsilon_0 + B_1 \varepsilon}{1 + B_1}, \quad \text{when } \varepsilon > k_0, \\ \varepsilon_1 &= \varepsilon - \varepsilon_2, \quad \varepsilon_2 = \varepsilon_0, \quad \text{when } \varepsilon \leq k_0; \end{aligned} \quad (10.7)$$

in all variants, $\varepsilon_{12} = \varepsilon_2$.

10.3.2 Unsteady-State Flow

The system of Eq. 10.5 is represented by first-order, linear differential equations. Let us first consider its analytical solution for step-wise input

$$\varepsilon_{\text{in}} = \begin{cases} 0 & \text{for } t \leq 0, \\ \varepsilon & \text{for } t > 0, \end{cases} \quad (10.8)$$

The first equation (10.5) transforms into the differential equation with separable variables

$$\frac{d\varepsilon'_1}{dt} = -(1 + B_1)E_1 \varepsilon'_1, \quad \varepsilon' = \varepsilon_1 - \frac{\varepsilon - \varepsilon_0}{1 + B_1}. \quad (10.9)$$

Its integration yields

$$\varepsilon_1 = \varepsilon F(t) + \varepsilon_0 \chi(t), \quad (10.10)$$

$$F(t) \equiv F_1(t) = \frac{1}{(1+B_1)} (1 - e^{-(1+B_1)E_1 t}), \quad \chi(t) \equiv \chi_1(t) = -F(t). \quad (10.10a)$$

The introduction of auxiliary functions F and χ is convenient for the subsequent application of the superposition method in the case of variable infiltration recharge, when $\varepsilon = f(t)$.

Upon the substitution of the leakage rate

$$\varepsilon_{12} = \varepsilon_0 + B_1 \varepsilon_1 = \varepsilon_0 + \frac{B_1}{1+B_1} (\varepsilon - \varepsilon_0) (1 - e^{-(1+B_1)E_1 t}) \quad (10.11)$$

the second equation (10.5) becomes

$$y' + fy = g(t), \quad (10.12)$$

where

$$y = \varepsilon_2 - \varepsilon_0, \quad f = E_2, \quad g(t) = \zeta E_2 (1 - e^{-(1+B_1)E_1 t}), \quad \zeta = \frac{B_1}{1+B_1} (\varepsilon - \varepsilon_0). \quad (10.12a)$$

Since this type of equation is rather common in problems of this kind, we will consider a method of its solution in more detail.

The equation (10.12) is linear with respect to y and its derivative y' . With y replaced by the product of two auxiliary functions (u and v) $y = uv$, the Eq. 10.12 becomes

$$u'v + u(v' + fv) = g(t). \quad (10.13a)$$

Since one of the auxiliary functions u or v can be chosen arbitrarily, we take v equal to a particular integral of equation $v' + fv = 0$. Now we obtain an equation of the form $u'v = g(t)$ to search for u . Separating variables in the first equation and integrating, we obtain the simplest nonzero particular integral: $v = e^{-ft}$. Substituting v into the second equation and solving it, we obtain u as a general integral of this equation: $u = \int g(t)e^{ft} dt + c$ (c is an integration constant). Finally:

$$y = uv = \left(\int g(t)e^{ft} dt + c \right) e^{-ft}. \quad (10.13b)$$

In our case,

$$u = \zeta e^{E_2 t} - \frac{\zeta E_2}{E_2 - (1+B_1)E_1} e^{(E_2 - (1+B_1)E_1)t} + c, \quad (10.13c)$$

$$y = uv \equiv \varepsilon_2 - \varepsilon_0 = \zeta - \frac{\zeta E_2}{E_2 - (1+B_1)E_1} e^{-(1+B_1)E_1 t} + c e^{-E_2 t}. \quad (10.13d)$$

The integration constant c is found from the condition $t = 0, \varepsilon_2 = 0$.

Finally, after simple transformation, we come to the relationship similar to Eq. 10.10

$$\varepsilon_2 = \varepsilon F(t) + \varepsilon_0 \chi(t), \quad (10.14)$$

$$F(t) \equiv F_2(t) = \frac{B_1}{1+B_1} \left[1 - \frac{1}{E_2 - (1+B_1)E_1} (E_2 e^{-(1+B_1)E_1 t} - (1+B_1)E_1 e^{-E_2 t}) \right],$$

$$\chi(t) \equiv \chi_2(t) = (1 - e^{-E_2 t}) - \frac{B_1}{1+B_1} \times \left[1 - \frac{1}{E_2 - (1+B_1)E_1} (E_2 e^{-(1+B_1)E_1 t} - (1+B_1)E_1 e^{-E_2 t}) \right]. \quad (10.14a)$$

When there is no water in the upper layer with $\varepsilon \leq \varepsilon_0$,

$$\varepsilon_2 = \varepsilon (1 - e^{-E_2 t}). \quad (10.15)$$

10.4 Time-Varying Infiltration

10.4.1 Computation Algorithm

The general solution for an arbitrarily varying input $\varepsilon(t)$ can be obtained by the superposition method, assuming that the function $\varepsilon_{in}(t) = \varepsilon(t)$ allows piecewise-homogeneous (multistep) representation, such that $\varepsilon^j = \varepsilon^{j-1} + \Delta\varepsilon^{j-1}$ ($\Delta\varepsilon^{j-1}$ is discharge increment at time t^{j-1} ; $j = 1, 2 \dots$ are the numbers of time intervals within which it is assumed $\varepsilon = \varepsilon^j = \text{const}$):

$$\varepsilon_{1,2} = \sum_{j=1}^N \Delta\varepsilon^{j-1} F_{1,2}(t - t^{j-1}) + \sum_{j=1}^N \Delta\varepsilon_K^{j-1} \chi_{1,2}(t - t^{j-1}), \quad (10.16)$$

where the increment $\Delta\varepsilon_K^{j-1}$ is chosen depending on the results of the current calculation of water balance in the upper horizon. Thus, if the upper horizon at time moment $t = t^j$ is filled with water, we have

$$\Delta\varepsilon_K^{j-1} = \varepsilon_0^j - \varepsilon_0^{j-1} (\varepsilon^{j-1}). \quad (10.16a)$$

Otherwise, if the upper horizon has been drained by moment $t = t^j$, we have

$$\Delta\varepsilon_K^{j-1} = \varepsilon^j - \varepsilon^{j-1} (\varepsilon_0^{j-1}), \quad (10.16b)$$

$\varepsilon_0^0 = 0$, $\varepsilon^0 = 0$. The values in parentheses in formulas (10.16a) and (10.16b) are the discharges assumed when a change from one regime to the other takes place at moment t^j .

Thus, as it has been already mentioned, in the case of variable infiltration, periods of filling of the upper layer with water can be followed by periods of its drying (resulting in its complete draining). The first equation of the system of equations (10.6) works in the periods when the upper horizon is filled with water, while during its drying, the recharge rate of the lower horizon does not depend on the characteristics of the separating layer and is governed by the second equation in (10.6). Thus, to assess the leakage conditions through the separating layer, one should take into account moisture balance in the upper horizon. If we assume the volume of infiltration water that has entered the water-bearing strata by moment t to be

$$W_1 = \int_0^t \varepsilon(t) dt, \quad (10.17)$$

then the first equation of the system (10.10) is valid at $W_1 > \int_0^t (\varepsilon_{12} + \varepsilon_1) dt$, otherwise, at $W_1 < \int_0^t (\varepsilon_{12} + \varepsilon_1) dt$, the second equation is valid. The above criterion relationships are to be checked during the numerical-analytical solution of appropriate problems. The total water discharge into the river within the streamtube (Fig. 10.3) is $Q_t = F\varepsilon_t = F(\varepsilon_1 + \varepsilon_2)$.

10.4.2 An Illustrative (Synthesized) Example

Consider synthesized function $\varepsilon(t)$ (Fig. 10.5), reflecting the abruptly heterogeneous distribution of precipitation over the basin within a 3-month period. The abrupt difference between kinetic constants E_1 and E_2 ($E_1 \gg E_2$) determines the specific behavior of the output functions ε_1 and ε_2 . Thus, it can be seen that, in dry periods, the total specific discharge ε_t is almost completely determined by water discharge from the system through the second layer; in the case of weak precipitation ($\varepsilon < \varepsilon_0$) with dry upper layer, water passes through the separating layer into the lower layer. Conversely, in short periods of intense infiltration, the top (first) bed is the main water vehicle, carrying considerable water masses out of the system. Overall, plots of total flow ε_t (Fig. 10.5) feature high peaks associated with flood periods; they are followed by dry periods during which the function ε_t ($\approx \varepsilon_2$) varies only slightly.

The model vividly illustrates a combination of fast and slow mechanisms of water exchange within closed drainage areas. Depending on the heterogeneity of precipitation distribution over time, the model “automatically” forms appropriate runoff components. The latter can be identified with the characteristics of near-surface and deep water exchange in such basins. Individual elements of the above analysis can be used to separate river hydrographs and as a basis for constructing mass balance models, which are considered below.

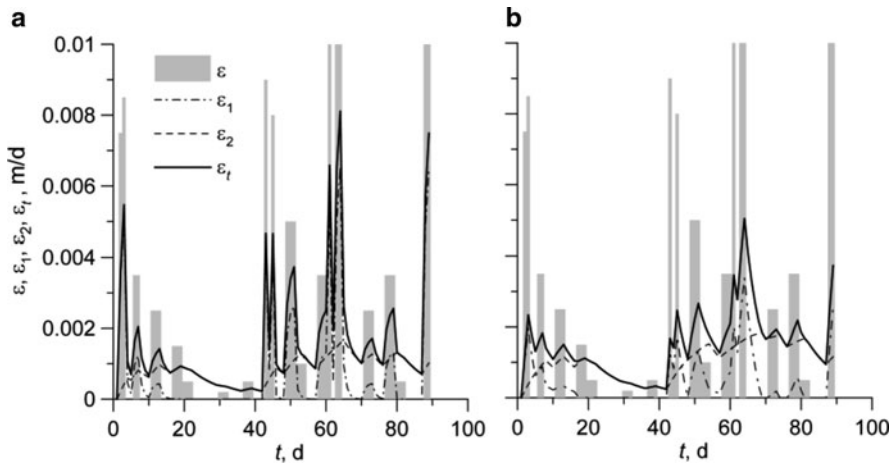


Fig. 10.5 The effect of kinetic constants E_1 and E_2 on flow rate variations in the discharge zone (with fixed $\varepsilon_0 = 0.002 \text{ m day}^{-1}$ and $B_1 = 0.1$). (a) $E_1 = 1.0 \text{ day}^{-1}$, $E_2 = 0.1 \text{ day}^{-1}$; (b) $E_1 = 0.2 \text{ day}^{-1}$, $E_2 = 0.1 \text{ day}^{-1}$

10.5 A Coupled Solution of Fluid Flow and Solute Transport Equations for Time-Independent Boundary Conditions

10.5.1 Steady-State Flow Field

The original system of mass balance equations in a two-layer system with $h_i = m_i = \text{const}$ (m_i is the mean flow thickness in the i th layer) can be written as

$$\begin{aligned} m_1 \phi_1 \frac{dC_1}{dt} + \varepsilon_1 C_1 + \lambda m_1 \phi_1 C_1 &= \varepsilon C_R - \varepsilon_{12} C_1, \\ m_2 \phi_2 \frac{dC_2}{dt} + \varepsilon_2 C_2 + \lambda m_2 \phi_2 C_2 &= \varepsilon_{12} C_1; \end{aligned} \quad (10.18)$$

here, the discharge characteristics are determined by (10.7). After their normalization relative to the storage capacity of the upper (first) layer $\varepsilon_i^* = \varepsilon_i / m_1 \phi_1$, $\varepsilon^* = \varepsilon / m_1 \phi_1$ and some transformations, the system of Eq. 10.18 can be presented in dimensionless form:

$$\begin{aligned} \frac{d\bar{C}_1}{d\tau} &= 1 - (1 + \bar{\lambda}) \bar{C}_1, \\ \frac{d\bar{C}_2}{d\tau} + (\bar{\varepsilon} + \bar{\lambda}) \bar{C}_2 &= \bar{\varepsilon} \bar{C}_1; \end{aligned} \quad (10.19)$$

here $\bar{C}_i = C_i/C_R$, $\tau = \varepsilon^* t$, $\bar{\lambda} = \lambda/\varepsilon^*$, $\bar{\varepsilon} = \sigma \varepsilon_2^*/\varepsilon^*$, $\sigma = m_1 \phi_1/m_2 \phi_2$, C_R is solute concentration in the infiltration water, λ is decay constant [T^{-1}] (see Sect. 3.2.1).

The solution of the first equation was obtained earlier (3.20, $C^0 = 0$):

$$\bar{C}_1 = \frac{C_1}{C_R} = F_1(\tau), \quad (10.20)$$

$$F_1(\tau) = \frac{1}{1 + \bar{\lambda}} \left(1 - e^{-(1 + \bar{\lambda})\tau} \right). \quad (10.20a)$$

Its substitution into the second equation of the system of Eq. 10.19 transforms this equation into

$$\frac{d\bar{C}_2}{d\tau} + (\bar{\varepsilon} + \bar{\lambda})\bar{C}_2 = \frac{\bar{\varepsilon}}{1 + \bar{\lambda}} (1 - e^{-(1 + \bar{\lambda})\tau}); \quad (10.21)$$

this equation corresponds to the ordinary differential equation (10.12) with $y = \bar{C}_2$, $f = \bar{\varepsilon} + \bar{\lambda}$, $g(\tau) = d(1 - e^{-b\tau})$; the constants b and d in the formula for $g(\tau)$ are defined as $b = 1 + \bar{\lambda}$, $d = \bar{\varepsilon}/(1 + \bar{\lambda})$.

The general solution of Eq. 10.21 has the form:

$$\bar{C}_2 = \frac{C_2}{C_R} = F_2(\tau), \quad (10.22)$$

$$F_2(\tau) = \frac{\bar{\varepsilon}}{(1 + \bar{\lambda})(\bar{\varepsilon} + \bar{\lambda})} \left(1 + \frac{\bar{\varepsilon} + \bar{\lambda}}{1 - \bar{\varepsilon}} e^{-(1 + \bar{\lambda})\tau} - \frac{1 + \bar{\lambda}}{1 - \bar{\varepsilon}} e^{-(\bar{\varepsilon} + \bar{\lambda})\tau} \right), \quad (10.23)$$

Under nonzero initial conditions,

$$C_i = C^0 + (C_R - C^0)F_i(\tau) \quad (i = 1, 2). \quad (10.24)$$

For steady-state flow conditions, the combine parameter $\bar{\varepsilon}$ can be predicted from the relationship $\bar{\varepsilon} = \sigma(\bar{\varepsilon}_0 + B_1)/(1 + B_1)$ (see Sect. 10.3.1).

10.5.2 Transient Flow Field

In the case of unconfined flow in a two-layer system (Fig. 10.3), one needs to take into account the degree to which aquifers are filled with water, manifesting itself in changes in groundwater heads (levels) $h_1 = h_1(t)$ and $h_2 = h_2(t)$; variations in those characteristics should be taken into account in solute mass balance equations.

Setting $S_{yi} = \phi_i$, we write the governing system of equations for normalized flows ($\epsilon^* = \epsilon/h_{10}\phi_1$, $\epsilon_i^* = \epsilon_i/h_{10}\phi_1$) as

$$\begin{aligned} d\bar{h}_1/dt &= (\epsilon^* - \epsilon_0^*) - \epsilon_1^*(1 + B_1), \\ d\bar{h}_2/dt &= \sigma(\epsilon_0^* - \epsilon_2^* + B_1\epsilon_1^*), \\ d\epsilon_1^*/dt &= E_1[(\epsilon^* - \epsilon_0^*) - \epsilon_1^*(1 + B_1)], \\ d\epsilon_2^*/dt &= E_2[(\epsilon_0^* - \epsilon_2^* + B_1\epsilon_1^*)], \\ \bar{h}_1 dC_1/dt + C_1 d\bar{h}_1/dt + \epsilon_1^* C_1(1 + B_1) + C_1 \epsilon_0^* &= \epsilon^* C_R, \\ \bar{h}_2 dC_2/dt + C_2 d\bar{h}_2/dt + C_2 \sigma \epsilon_2^* &= \sigma(\epsilon_0^* + B_1 \epsilon_1^*) C_1, \end{aligned} \quad (10.25)$$

where $\bar{h}_1 = h_1/h_{10}$, $\bar{h}_2 = h_2/h_{20}$, $\sigma = \frac{h_{10}\phi_1}{h_{20}\phi_2}$, h_{10} and h_{20} are the initial thicknesses of water layer in the first and second aquifers; solute decay in the water-bearing system is neglected ($\lambda = 0$).

Assuming

$$\frac{d\bar{h}_1}{dt} = \frac{1}{E_1} \frac{d\epsilon_1^*}{dt} \text{ and } \frac{d\bar{h}_2}{dt} = \frac{\sigma}{E_2} \frac{d\epsilon_2^*}{dt}, \quad \bar{h}_1 = 1 + \frac{1}{E_1} \epsilon_1^* \text{ and } \bar{h}_2 = 1 + \frac{\sigma}{E_2} \epsilon_2^*,$$

we transform the system of Eq. 10.25 into

$$\begin{aligned} \left(1 + \frac{\bar{\epsilon}_1}{\bar{E}_1}\right) \frac{d\bar{C}_1}{d\tau} &= 1 - \bar{C}_1, \\ \left(1 + \frac{\bar{\epsilon}_2}{\bar{E}_2}\right) \frac{d\bar{C}_2}{d\tau} &= \sigma(\bar{\epsilon}_0 + B_1 \bar{\epsilon}_1)(\bar{C}_1 - \bar{C}_2), \end{aligned} \quad (10.26)$$

where $\bar{\epsilon}_i = \epsilon_i^*/\epsilon^*$, $\bar{E}_i = E_i/\epsilon^*$. The first equation is an ordinary, first-order differential equation with separable variables. Its solution is

$$\bar{C}_1(\tau) = 1 - \exp\left(-\int_0^\tau \frac{d\tau}{1 + \bar{\epsilon}_1/\bar{E}_1}\right). \quad (10.27)$$

Upon integration, we finally obtain

$$\bar{C}_1(\tau) = 1 - \left\{ e^{-\frac{\tau}{1+\bar{\epsilon}^*}} \left[1 + \bar{\epsilon}^* \left(1 - e^{-(1+B_1)\bar{E}_1\tau} \right) \right]^{-n} \right\}, \quad (10.28)$$

where

$$\bar{\epsilon}^* = \frac{1 - \bar{\epsilon}_0}{(1 + B_1)\bar{E}_1}, \quad n = \frac{1}{(1 + \bar{\epsilon}^*)(1 + B_1)\bar{E}_1}, \quad \bar{\epsilon}_0 = \frac{\epsilon_0}{\epsilon}. \quad (10.28a)$$

The second Eq. 10.26 has the form similar to Eq. 10.12, where, however, the function f is a complicated function of dimensionless time:

$$y' + f(\tau)y = g(\tau), \quad (10.29)$$

where

$$y = \bar{C}_2, \quad f(\tau) = \frac{\sigma(\bar{E}_0 + B_1\bar{E}_1)}{(1 + \bar{E}_2/\bar{E}_2)}, \quad g(\tau) = \frac{\sigma(\bar{E}_0 + B_1\bar{E}_1)}{(1 + \bar{E}_2/\bar{E}_2)}\bar{C}_1. \quad (10.29a)$$

The general solution of Eq. 10.29 has the form (Kamke 1977)

$$y = e^{-F} \left(c + \int g(t)e^F d\tau \right), \quad F(\tau) = \int f(\tau)d\tau, \quad (10.30)$$

where the constant, c , can be found from the condition $y(\tau = 0) = 0$.

The explicit solution (10.30) has a complicated form; therefore, we well restrict ourselves to giving the results of numerical calculations (Fig. 10.6).

The calculations were carried out within a wide variation range of kinetic parameters $\bar{E}_1$ and $\bar{E}_2$, the values of other variables being fixed (Fig. 10.6). These calculations show that small deviations of curves from the values obtained from the steady-state flow model (Sect. 10.5.1) were recorded at very small values of $\bar{E}_i$ (<1). In this interval of values, the breakthrough curves were found to lag behind the curves obtained for steady-state flow, an effect resulting from water accumulation in the system, facilitating further dilution of solute.

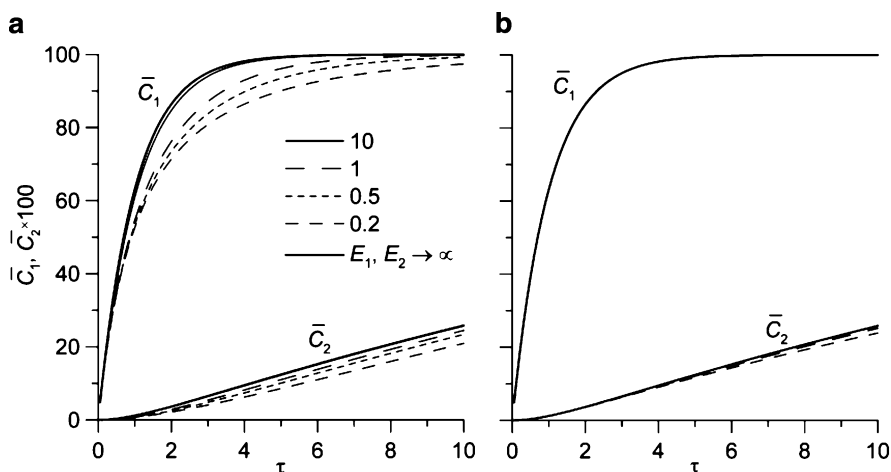


Fig. 10.6 The effect of transiency of groundwater flow on the character of concentration curves $\bar{C}_1$ and $\bar{C}_2$. The calculations were carried out (a) at different values of E_1 with fixed $E_2 = 100$; (b) at different E_2 for fixed $E_1 = 100$. Other parameters were as follows: $\bar{E}_0 = 0.2, B_1 = 0.2, \sigma = 0.1$

10.6 A Coupled Solution of Fluid Flow and Solute Transport Equations for Time-Variable Input Functions

10.6.1 Numerical–Analytical Solution Algorithm

In the reservoir-type, two-layer model with piece-wise representation of functions $C_R(t)$ and $\varepsilon(t)$, any concentration value $C_{1,2}^i$ (at time t^i) can be found explicitly given the preceding concentration $C_{1,2}^{j-1}$ (at time t^{j-1}):

$$C_{1,2}^i = C_{1,2}^{i-1} + (C_R^i - C_{1,2}^{i-1}) F_{1,2}(t^i - t^{i-1}), \quad (10.31)$$

where the basic functions $F_{1,2}(t)$ are defined by (10.20a) and (10.23).

Upon a series of successive substitutions, we obtain a generalized formula for the first layer

$$C_1^i = C_R^0 + \sum_{j=1}^i (C_R^j - C_R^{j-1}) \left[1 - \exp \left(- \sum_{k=j}^i \varepsilon^{*k} (t^k - t^{k-1}) \right) \right]; \quad (10.32)$$

here $\varepsilon^{*k} = \varepsilon^k / m_1 \phi_1$, $t^0 = 0$, C_R^0 is the initial concentration; to simplify the representation of formulas, we assume $\lambda = 0$.

If it is only infiltration rate that changes over time with $C_R = \text{const}$, the formula (10.32) becomes

$$C_1^i = C_R^0 + (C_R - C_R^0) \left[1 - \exp \left(- \sum_{k=1}^i \varepsilon^{*k} (t^k - t^{k-1}) \right) \right]. \quad (10.33)$$

If the infiltration rate is constant ($\varepsilon = \text{const}$), while the concentration varies over time, we have

$$C_1^i = C_R^0 + \sum_{j=1}^i (C_R^j - C_R^{j-1}) (1 - \exp[-\varepsilon^*(t^i - t^{j-1})]), \quad (10.34)$$

i.e., we come to formula (3.23) for the particular case $\lambda = 0$.

Expressions for the function C_2^i can be obtained similarly. An alternative is to determine the function C_2^i given the values of C_1^i and ε_2^{*i} :

$$C_2^i = C_R^0 + \sum_{j=1}^i (C_1^j - C_1^{j-1}) \left[1 - \exp \left(- \sum_{k=j}^i \sigma \varepsilon_2^{*k} (t^k - t^{k-1}) \right) \right], \quad (10.35)$$

where $\sigma \varepsilon_2^{*k} = \varepsilon_2^k / m_2 \phi_2$.

10.6.2 An Illustrative (Synthesized) Example

The distribution given in Fig. 10.5 is used as a synthesized input $\varepsilon(t)$. We assume that solute concentration in the upper layer C_1 corresponds to the value $C_R = \text{const}$, its background concentration being $C_R^0 = 0$. When calculating by formula (10.16), we assume that the function ε_2 can be derived from the condition of water balance in the system (see Sect. 10.4.1). The redistribution of groundwater flow in the case of dramatically uneven infiltration results in the formation of a fast, ε_1 , and slow, ε_2 , components of the total characteristic ε , where in the general case, because of the nonstationarity of the process, we have $\varepsilon_1 + \varepsilon_2 \neq \varepsilon$.

The plots in Fig. 10.7 suggest that the rate of concentration growth in the second layer, C_2 , depends, other conditions being the same, on the kinetic constant E_1 , governing the degree to which the upper layer is filled with water. As far as the period within which water is retained in the upper layer and the rate of leakage ε_{12} increase with decreasing E_1 , the breakthrough curve C_2 lies beneath the curve calculated with larger E_2 .

Further, Fig. 10.7 also gives a curve obtained with the mean value of groundwater infiltration recharge (in this case, $\varepsilon_{av} = 0.00172$ m/day). Since $\varepsilon_{av} < \varepsilon_0$, the upper layer will not fill and the entire infiltration water will pass into the underlying aquifer; the amount of the solute delivered by infiltration water into this aquifer will be larger. Accordingly, the concentration in this case will be appreciably greater than C_2 , calculated earlier for the case of uneven infiltration recharge of the water-bearing strata.

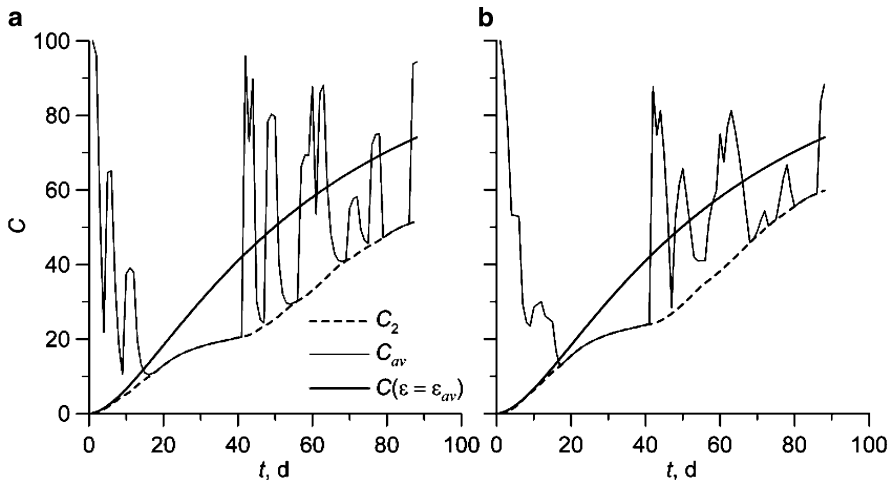


Fig. 10.7 Variations of concentration functions C_2 , C_{av} and $C(\varepsilon = \varepsilon_{av})$ at constant solute concentration in the infiltration water $C_R = 100$; $m_2 \phi_2 = 0.1$ m. The hydraulic characteristics of the model are taken in accordance with calculations made before: (a) Fig. 10.5a and (b) Fig. 10.5b

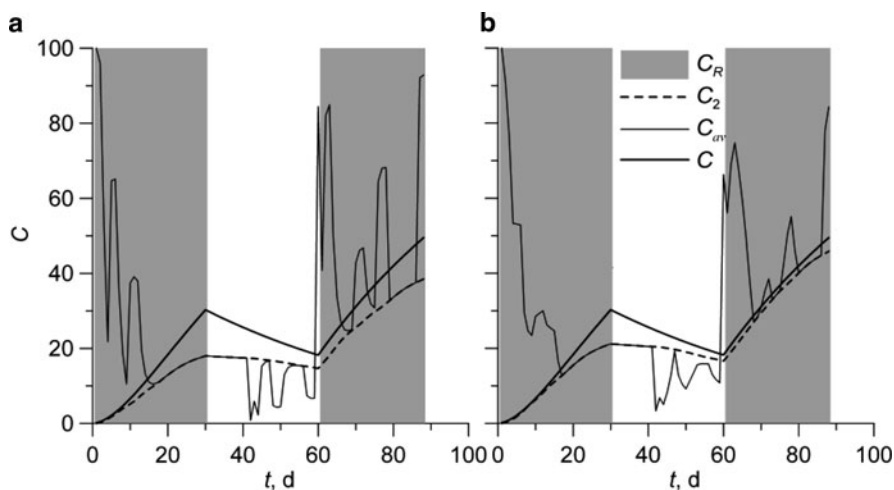


Fig. 10.8 The character of variations in the concentration functions C_2 , C_{av} and $C(\epsilon = \epsilon_{av})$ when solute concentration in infiltration water varies over time. $C_R \neq \text{const}$, $m_2\phi_2 = 0.1$ m. The hydraulic characteristics of the model are taken in accordance with calculations made before: (a) Fig. 10.5a and (b) Fig. 10.5b

Thus, the fractionation of infiltration flow, which is inherent in this reservoir-type model, causes redistribution of solute in the system. Therefore, estimates derived from models with time-averaged values of ϵ may lead to errors in predicting mass (chemical) balance.

Figure 10.7 also gives curves for mean solute concentration at the outlet from the system, $C_{av} = (C_1\epsilon_1 + C_2\epsilon_2)/(\epsilon_1 + \epsilon_2)$. The abrupt variations in function $C_{av}(t)$ are also a consequence of infiltration water fractionation. The maximal values of $C_{av}(t)$ correspond to flood periods, when the solute is mostly discharged from the system through the upper aquifer; in low-flow periods, $C_{av}(t)$ are minimal and equal to solute concentration in the bottom layer, C_2 .

Finally, Fig. 10.8 reflects the tendencies in solute concentration variations in the two layer formation in the case when function C_R varies over time. In particular, as can be distinctly seen from these plots, water infiltration in the periods when $C_R = 0$ leads to dilution of the solute (that have entered the system when $C_R = 100$) in the bottom aquifer.

10.7 Runoff, Infiltration, and Groundwater Recharge

In this section, we will focus on the second basic model, assuming that a fraction of rainfall flows over a land surface from higher to lower elevation. This phenomenon is known as overland runoff. Overland flow contributes to quick response in the stream and is an additional pathway for chemical component transport.

10.7.1 Water Budget

In accordance with the conceptual scheme (Fig. 10.9), partitioning of precipitation P into two components, r and i , takes place at the atmosphere–soil interface; continuity implies that

$$P = r + i, \quad (10.36)$$

where r is the runoff; $i \equiv i_a$ is the actual infiltration; all dimensions are $[LT^{-1}]$. Surface runoff is the water flow, which occurs when excess water from rain, snowmelt, or other sources flows over the land. Infiltration is defined as the process of water penetration into the soil. The infiltration is controlled by many factors, such as the precipitation characteristics, rate of water application, antecedent moisture in the soil, soil hydraulic properties, topography, and others (Stephens 1996; Weight 2008).

As might be intuitively expected, the slope of the land surface can also indirectly impact the redistribution of water at the air–soil interface (Williams et al. 1998). Indeed, the slope controls the amount of time the water will be available for infiltration. Thus, a steep slope will generate intensive runoff and the surface water will be available for infiltration during a restricted period, i.e., the rain may not have the time to infiltrate. In contrast, a gentle slope will have lesser impact on the infiltration process due to decreased runoff. Besides there are direct physical effects of slope on infiltration that require considering a new extended formulation of the governing equations for infiltration processes in the soil domain (Chen and Young 2006). In our analysis, taking into consideration the conceptual character of the analyzed models, we will neglect the influence of variations in the degree of land sloping on infiltration and runoff generation.

Equation 10.36 can be regarded as the limiting variant of kinematic wave equation

$$\frac{\partial h}{\partial t} + \nabla Q = P - i. \quad (10.36a)$$

In a quasi-one-dimensional and steady-state representation of the process $\nabla Q = r$ and $\partial h / \partial t = 0$; Q is the depth-averaged surface water discharge $[L^2T^{-1}]$; h is the surface ponding depth $[L]$.

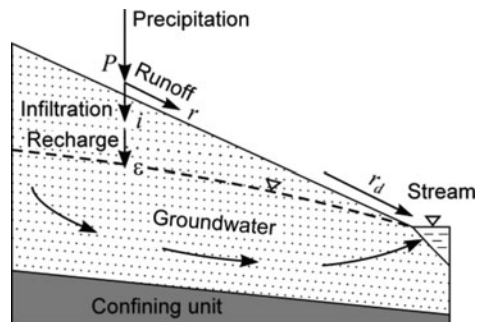


Fig. 10.9 Conceptual diagram of precipitation partitioning

The elimination of $\partial h/\partial t$ from the equation is equivalent to assuming the response of the river to precipitation to be instantaneous. Actually, the discharge of surface runoff into the river network that drains the catchment area takes place with a time lag after the precipitation event. This is due to the morphological heterogeneity of the relief and the need for water flow on the surface to cover a certain distance. By analogy with groundwater flow processes described by reservoir models (see Sect. 10.2), the finite flow velocity can be accounted for in the following kinetic equation:

$$\frac{dr_d}{dt} = E_d(r - r_d), \quad (10.36b)$$

where E_d is some kinetic coefficient [T^{-1}], depending on the geomorphological and landscape conditions in the catchment area; r_d is flow velocity, determining the discharge into the river [LT^{-1}]. Numerical integration of (10.36b) with known function $r = r(t)$ allows one to evaluate r_d .

In the classical concept, surface runoff formation, resulting from land surface inundation (ponding), takes place in the case where precipitation rate P is greater than the rate of moisture imbibition i . The imbibition process (moistening of the near-surface soil layer) depends on the hydraulic and capillary characteristics of the soil. The theory of the process has been developed rather well; in particular, criteria were obtained for assessing the descending moisture flux from the surface at different stages of the process and the time required for surface water layer to form. However, considering the high variability of properties of near-surface deposits and variations in landscape conditions, the direct practical use of the obtained analytical solutions often faces considerable difficulties. Therefore, phenomenological models are more often used to describe surface runoff formation.

Moisture motion in the soil and the aeration zone under the effect of gravity and capillary forces leads to water supply to phreatic water table with a rate assumed to be equal to its recharge rate ε . At the same time, moisture is being removed from the aerated zone through evaporation and moisture consumption by plants, as is reflected in the generalized rate of actual evapotranspiration ε_{EPT} .

The processes of infiltration, percolation, and evapotranspiration are accompanied by changes in saturation (water content) within the vadose zone. We assume the fluxes i , ε , and ε_{EPT} in the general case to be interrelated and their rate to determine the *mean* moisture content of the covering sediments θ_a [L^3L^{-3}] in some *active soil layer* with effective thickness m_a . In this case, the basic structure of a vertically averaged model of soil moisture is the differential equation describing the rate of change in soil moisture content as the sum of input and losses associated with the active soil layer (Rigby and Porporato 2006):

$$m_a \frac{d\theta_a}{dt} = i - \varepsilon - \varepsilon_{EPT}. \quad (10.37)$$

One of the main difficulties in the subsequent development is due to the need to define the functions r , ε , and ε_{EPT} , whose form is ambiguous and depends on some hydrophysical, landscape, and climate characteristics. Therefore, without claiming

the reasoning to cover the general case, we restrict ourselves to a demonstration analysis based on more or less established and accepted (verified) models of runoff formation and moisture transfer.

10.7.2 *Infiltration Models and Conceptual Scenarios for Runoff Generation*

The development of dynamic *rainfall–runoff* models, which would predict the partitioning of water during precipitation cycles between land surface, subsurface environment, and stream within a watershed, is essentially based on the infiltration theory and related infiltration models. Many approaches have been presented to solve the problem of water infiltration into soil. Comprehensive reviews of the historic development of infiltration theory and a number of models can be found in numerous research publications (Hopmans et al. 1997; Williams et al. 1998; Mishra et al. 2003; Chahinian et al. 2005; Erickson and Stefan 2007; Dashtaki et al. 2009; Bear and Cheng 2010).

Infiltration models can be classified, in general, into three groups (Mishra et al. 2003): (1) physically-based, (2) semi-empirical, and (3) empirical. Several physically-based models relying on the mass conservation law and the Darcy law have been considered in Sect. 2.1.3. The parameters of these infiltration models usually have physical meaning; they can be derived from soil physical properties. However, when applied to field-obtained infiltration data, the physically-based models are often used in a manner effectively similar to the empirical models because a number of assumptions are typically violated (Hopmans et al. 1997). Two models and their modifications derived from physical considerations have been analyzed in Sects. 2.1.3.3 (Philip 1957a, b, c) and 2.1.3.5 (Green and Ampt 1911).

Semi-empirical models employ simple forms of continuity equation (often spatially lumped) and simple hypotheses on the infiltration rate relation (Mishra et al. 2003). These models are a compromise between empirical and physically based models. An example of semi-empirical model will be presented in Sect. 10.8.

The empirical models usually have a simple mathematical form as a function of time; their parameters are derived by means of curve fitting of the selected equation to actual measurements of cumulative infiltrated water (Dashtaki et al. 2009).

To continue the discussion on the applicability of a particular infiltration model for describing the overall rainfall–runoff process, we must answer the question what other physical phenomena are involved in converting rainfall to runoff?

Following the classical conceptual scheme, we will consider a semi-infinite permeable soil profile (with a homogeneous initial water content distribution), which is subject to precipitation with a constant rainfall rate, P . Depending on the structure of the infiltration function, $i(t)$, which can be considered as the *potential infiltration rate*, the relationship between precipitation rate (rainfall intensity), P , and saturated hydraulic conductivity, k_s , and the initial soil water content, θ_i , the process can follow *three basic scenarios* (Stephens 1996; Weight 2008). These scenarios can be

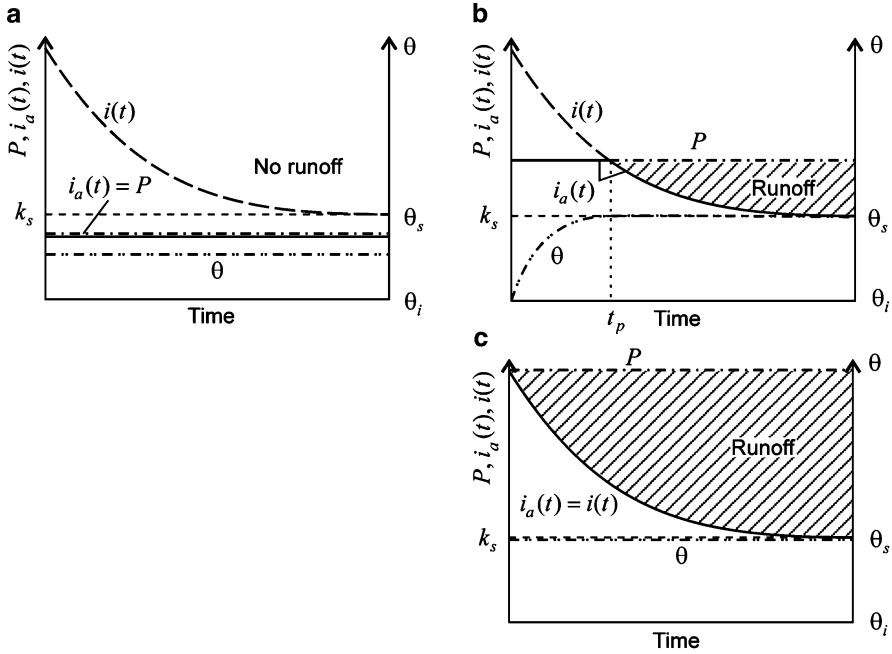


Fig. 10.10 Infiltration rate $i_a(t)$ dependence on rain intensity P

illustrated by the behavior of the two flow components (Fig. 10.10), $i_a(t)$, that is, the *actual/observed infiltration rate*, and P , during constant precipitation. Changes in the average water saturation, θ_a , of the soil near the surface (Fig. 10.10) shows a tendency toward changes in relationship between capillary and gravity forces.

The first scenario is realized, if the rainfall intensity is less than the magnitude of the saturated hydraulic conductivity of the soil. Under this condition, all the water supplied is free to infiltrate and none is available for runoff (Fig. 10.10a). In other words, water can infiltrate into soil as quick as it is applied, and the supply rate determines the actual infiltration rate. Mathematical formalization of the process is as follows:

$$i_a(t) = P \leq i(t). \quad (10.38)$$

The second scenario is associated with the case in which rainfall rate exceeds the saturated hydraulic conductivity but is less than the initial infiltrability of the relatively dry soil. During this initial period, infiltration is limited by rainfall intensity rather than potential infiltration rate (Fig. 10.10b). The soil initially takes up the rain-water as rapidly as it falls, owing to the strong capillary forces in the soil (Weight 2008). An increase in soil moisture content during the further infiltration facilitates a decrease in the suction capillary pressure and, accordingly, a drop in the rate of actual imbibition $i_a(t)$, which tends to the rate $i(t)$. After the time $t = t_p$ at which the infiltration rate equals the rainfall intensity, $i_a(t) = P$, land ponding occurs: the

free water tends to accumulate over the soil surface providing a condition for runoff generation. Mathematically, the actual infiltration rate for this scenario should then be of the form:

$$i_a(t) = \begin{cases} P & 0 \leq t \leq t_p, \\ i(t - t_p) & t > t_p. \end{cases} \quad (10.39)$$

Time t_p can be easily estimated for a known analytical function of potential infiltration by setting $P = i(t_p)$.

Finally, the third scenario has to do with the case where rain intensity is much higher than the saturated hydraulic conductivity (Fig. 10.10c). Then the runoff will begin almost instantly:

$$i_a(t) = i(t) \leq P. \quad (10.40)$$

Several conclusive comments are as follows. The infiltration rate before ponding is determined by the rainfall intensity, and the higher the precipitation rate, the sooner runoff commences. However, the sensitivity of an infiltration system to rainfall intensity is not as great as its sensitivity to the initial negative pore water pressure distribution and the hydraulic properties of the soil (Ng and Menzies 2007). Therefore, the initial soil water content, controlling the pressure head, and the saturated hydraulic conductivity of the soil are the primary factors affecting the soil water infiltration process. The wetter the soil initially, the lower will be the initial infiltrability (due to a smaller suction gradient), and a constant infiltration rate will be attained more quickly; again, the higher the saturated hydraulic conductivity of the soil, the higher the infiltrability (Williams et al. 1998). Generally, whenever water is ponded over the soil surface, the rate of water application exceeds the soil infiltrability.

In principle, Eqs. 10.38–10.40 can be used to develop simplified rainfall–runoff models by solving equation of flow in the unsaturated zone with respect to the potential infiltration rate $i(t)$. Two methods that estimate infiltration function $i(t)$ are the Philip's (Sect. 2.1.3.3) and Green and Ampt (Sects. 2.1.3.5 and 2.1.3.6) methods. However, for the future analysis we selected a model treating $i(t)$ as a semi-empirical function with empirical land-use coefficients.

10.8 A Modified SCS-CN Model

10.8.1 A Basic Semi-Empirical Formula for Runoff Calculation

The model was developed by the U.S. Department of Agriculture Soil Conservation Service (SCS), 1972 (USDA 1986; Stone et al. 2001; Woodward et al. 2003; Chahinian et al. 2005) for estimating a rainfall–runoff relationship for watersheds. The Soil Conservation Service Curve Number (SCS-CN) method is direct runoff estimation through an empirical equation that requires rainfall and a watershed coefficient as inputs. The model can also be used to estimate rainfall–runoff discharge, and can be converted to an infiltration equation. SCS-CN theory is based

on the fact that direct runoff, after initial infiltration occurs, depends on land cover, land use, soil type, and antecedent moisture conditions of surface soil. Several accompanying tables have been developed in association with empirical equations.

The SCS-CN method assumes that there is some rainfall amount, I_a (initial abstraction), for which no runoff will occur. The potential runoff therefore is $P - I_a$. After runoff begins, the additional depth of water retained in the watershed, F_a , is less than or equal to some potential maximum retention, $S_{\max}$. The SCS method assumes that the ratios of the two actual to the two potential quantities are equal (Erickson and Stefan 2007; Shi et al. 2009), i.e.,

$$\frac{F_a}{S_{\max}} = \frac{r}{P - I_a}. \quad (10.41a)$$

From continuity,

$$P = r + I_a + F_a. \quad (10.41b)$$

Combining (10.41a) and (10.41b) and solving for r gives

$$r = \frac{(P - I_a)^2}{(P - I_a) + S_{\max}}. \quad (10.42)$$

Field studies have shown that in the first approximation: $I_a = 0.2S_{\max}$.

Empirical studies indicate that the potential maximum retention can be estimated as (USDA 1986):

$$S_{\max} = \frac{1000}{\text{CN}} - 10, \quad (10.42a)$$

where CN is a runoff curve number, which is a function of land use, antecedent soil moisture, and other factors affecting runoff and retention in a watershed (Erickson and Stefan 2007); CN varies from 0 (the soil imbibes all rainfall) to 100 (no imbibitions occurs). The use of formula (10.42a) implies that the calculated variable $S_{\max}$ has the dimension of inch/day. In the analysis that follows, we will mostly use more common measurement units: m for length [L] and day for time [T].

Shestakov and Pozdniakov (2003), with references to earlier studies, give the following CN intervals for four typical hydrologic soil groups:

Soil	CN	Soil	CN
Sand	40–60	Silt loam	75–85
Sandy loam	60–75	Silty clay loam	85–98

They allow one to determine the curve number for different types of vegetation-covered soils and use the obtained value to evaluate $S_{\max}$ by using (10.42a), which has been written for some annually averaged moisture content of the soil layer. It is clear, however, that the depth of surface runoff layer is related with the soil moisture content immediately before the specific event in some season of the year.

The authors of the study mentioned above (Shestakov and Pozdniakov 2003) note that the tentative value $S_{\max}$ tends to the hydraulic conductivity of near-surface deposits.

A major weakness is the sensitivity of estimated runoff to errors in the selection of the curve number (CN). Changes of about 15–20% in the curve number double or halve the total estimated runoff (Boughton 1989). Usually the standard SCS-CN method underestimates and overestimates infiltration for large runoff events (Erickson and Stefan 2007; Shi et al. 2009). Moreover, the technique is intended primarily for estimating the hydrological consequences of short-time atmospheric precipitation (with a sufficiently large rate – about 10 mm/day), and the consequences of such event are by no means related with the previous one, i.e., it is a priori assumed that, between rain events, the soil returns to its initial state, characterized by parameter $S_{\max}$. However, the statistical character of function P determines the strong time variations in soil moisture content; therefore, strictly speaking, the potential maximum retention is not constant for the catchment area. It varies both within a year and over many-year period, such that the response of the system in any moment depends on the history of previous events. This limits the practical possibility to apply the approach described above.

In this work, we propose to replace the constant $S_{\max}$ in the basic relationship (10.42) by the current (time-dependent) characteristic S , evaluated based on the degree of soil moisture saturation (Shestakov and Pozdniakov 2003):

$$S = S_{\max} (1 - \bar{\theta}), \quad (10.43)$$

where $\bar{\theta} = (\theta - \theta_r) / (\theta_s - \theta_r)$ is the normalized volumetric water content, θ_s is the saturated volumetric water content (maximum water content), θ_r is the residual volumetric water content; When $\theta = \theta_r$, $S = S_{\max}$, i.e., the parameter $S_{\max}$ determines moisture imbibition by dry soil, so there is no full analogy with SCS-CN model. A quite similar approach has been suggested (Chahinian et al. 2005) for using the SCS-CN model in calibration mode.

10.8.2 Basic Relationships for Flow Characteristics

The SCS-CN model can be expressed as an infiltration equation. As the potential infiltration rate $i(t)$ is equal to $P - r$, we can rewrite (10.42) as

$$i(t) = \frac{PI_a + PS - I_a^2}{P - I_a + S}. \quad (10.44)$$

Equation 10.44 is valid for $P > I_a$, otherwise, $i_a(t) = P$, or following (10.39)

$$i_a(t) = \begin{cases} i(t) & \text{for } P > I_a, \\ P & \text{for } P < I_a, \end{cases} \quad (10.45)$$

$S = S(\theta)$, and $I_a = 0.2S$.

Consider other terms of the right-hand part of (10.37).

Percolation recharge, ϵ , is dependent on the soil's saturation and hydraulic conductivity. If gravity is assumed to be the only vertical driving force of percolation

(i.e., there are no capillary forces), the percolation is equal to the unsaturated hydraulic conductivity, k , of the soil and is given as (Beckers and Alila 2004)

$$\varepsilon = k(\bar{\theta}). \quad (10.46)$$

As it was mentioned in Chap. 2, Averjanov's (2.10) and van Genuchten's (2.13) relationships are most commonly used.

There exists a wide variety of approaches to evaluating soil moisture evapotranspiration (ε_{EPT} is the third flow characteristic in the balance Eq. 10.37). This is due to the complicated character of relationship between ε_{EPT} and some soil characteristics, such as potential physical evaporation, potential transpiration, soil moisture state, temperature, precipitation, etc.

The simplest relationship,

$$\varepsilon_{EPT} = \varepsilon_{PE} \bar{\theta}, \quad (10.47)$$

was substantiated in Shestakov and Pozdniakov (2003); here ε_{PE} is potential evaporation, understood as the maximal possible evaporation under the conditions when the moisture reserves available for evaporation are unlimited. The paper mentioned above gives a detailed review of other analytical expressions relating functions ε_{EPT} and ε_{PE} .

The reasoning and analytical expressions considered above allow the Eq. 10.37 to be written in the following generalized form:

$$\frac{d\bar{\theta}}{dt} = \begin{cases} \frac{\bar{P}I_a + \bar{P}\bar{S}(\bar{\theta}) - I_a^2}{\bar{P} - I_a + \bar{S}(\bar{\theta})} - \bar{k}(\bar{\theta}) - \bar{\varepsilon}_{EPT} & \text{for } \bar{P} > \bar{I}_a, \\ \bar{P} - \bar{k}(\bar{\theta}) - \bar{\varepsilon}_{EPT} & \text{for } \bar{P} < \bar{I}_a; \end{cases} \quad (10.48)$$

here $\bar{P} = P/m_v$, $\bar{S} = \bar{S}_{\max}(1 - \bar{\theta})$, $\bar{S}_{\max} = S_{\max}/m_v$, $\bar{k}(\bar{\theta}) = k(\bar{\theta})/m_v$, $\bar{I}_a = 0.2\bar{S}(\bar{\theta})$, $\bar{\varepsilon}_{EPT} = \varepsilon_{EPT}/m_v$, $m_v = m_a(\theta_s - \theta_r)$.

The equation (10.48) is nonlinear. Its solution with respect to the dimensionless moisture content function can be obtained numerically (below we use an implicit finite-difference scheme for solving the differential Eq. 10.48). The evaluation of $\bar{\theta}$ allows one to determine $\bar{S}$ (10.43) and, hence, both the surface runoff depth and the infiltration recharge rate.

10.8.3 Concentration Response Function

One of the advantages of the discussed above model is the fact that it yields the daily distribution of major characteristics, r , ε and θ , allowing the model to be used for detailed analysis of the formation of the chemical and isotopic composition of surface water and groundwater. In particular, the distribution $\varepsilon(t)$ can be considered as an input function for searching the solution of mass balance and transport problems.

Numerous examples of joint use of long-term monitoring data on the isotopic composition of atmospheric and river water are available in the literature, allowing one to study water cycles of the drainage basins of large and small rivers (Rozanski et al. 2000). In this section and following illustrative example, we analyze the possibility to predict seasonal variations in the isotopic composition of river water that forms from precipitation falling onto a watershed under study. Such analysis will be of exceptionally conceptual character.

Suppose that precipitation delivers a dissolved solute to soil surface. Conceptualizing the vadose zone as a zero-dimensional black box represented by a simplest lumped-parameter model, we can determine the mean velocity of solute vertical migration, $u(t)$, in any moment, t ,

$$u(t) \approx \varepsilon/\theta, \quad (10.49)$$

where $\varepsilon = \varepsilon(t)$ and $\theta = \theta(t)$ are infiltration rate and mean moisture content of the soil profile. Both functions, determining $u(t)$, are complicated functions of soil moistening regime, which, in its turn, is controlled by soil hydraulic and capillary properties and the partitioning of atmospheric moisture under statistical character of precipitation distribution.

Suppose that variations in solute concentration in atmospheric water can be approximated by a step-wise function, as it is made, for example, in the description of cyclic variations in concentrations of stable isotopes of ^{18}O and D or the unstable isotope ^3H . Now the time of motion of each elementary “parcel” ΔC_j in the vadose zone will depend on the characteristics mentioned above. The moment t_i^j when the j th parcel reaches the lower boundary of the vadose zone (with a thickness of m_A), given that it arrives onto the soil surface at time t_i , can be found from the integral relationship

$$m_A = \int_{t_i}^{t_i^j} u(t - t_i) dt. \quad (10.50)$$

The migration conditions of each concentration package are individual because of the statistical character of variations in system parameters. Therefore, in the general case, the parcels should contract or extend in time at the outlet boundary. Thus, the breakthrough concentration function will change.

10.8.4 Illustrative Examples

10.8.4.1 Synthesized Example 1

Figure 10.11 gives plots of major flow characteristics evaluated for step-wise precipitation input: a 15-day period of intense atmospheric precipitation ($P_1 = 0.1$ m/day) gives way to a drier period ($P_2 = 0.01$ m/day) with the same duration (considering the illustrative character of the example, we will not focus on the values

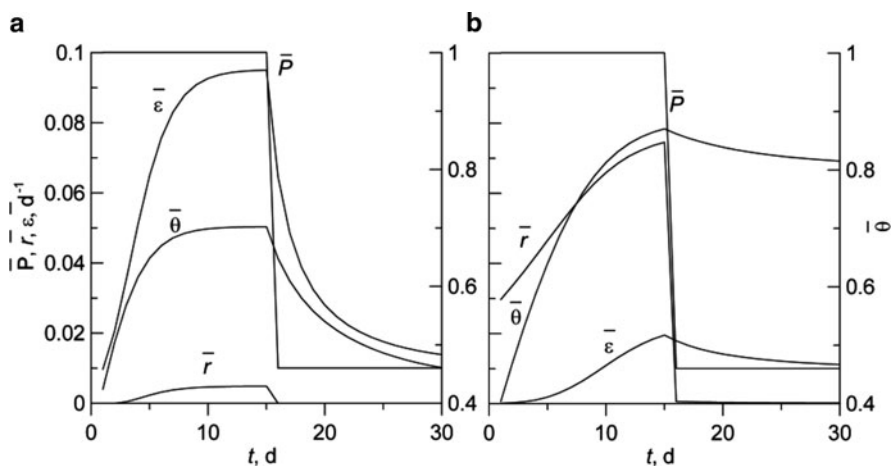


Fig. 10.11 Plots of functions $\bar{P}(t)$, $\bar{v}(t)$, $\bar{\epsilon}(t)$, and $\bar{\theta}(t)$. (a) Sand deposits ($k_s = S_{\max} = 1$ m/day, $n = 2.22$); (b) loamy deposits ($k_s = S_{\max} = 0.2$ m/day, $n = 1.54$); other parameters: $m_a = 3.33$ m, $\theta_r = 0.1$, $\theta_s = 0.4$, $\theta_0 = 0.2$

of these synthesized variables). Calculations have been carried out for two characteristic types of blanket deposits, represented by sands (Fig. 10.11a) and loams (Fig. 10.11b): for sands, we assumed $k_s = S_{\max} = 1.0$ m/day, $n = 2.22$ (the exponent in van Genuchten's formula (2.13) for unsaturated hydraulic conductivity); for loams, $k_s = S_{\max} = 0.2$ m/day, $n = 1.54$. The values of θ_0 , θ_r , and θ_s were taken the same for the two calculation variants (see the caption to Fig. 10.11). All flow characteristics (P , v , and ϵ) are normalized with respect to the reduced capacity of the active soil layer m_v (see formula (10.48)); in this example $m_v = 1$ m.

Analysis of the above results shows that precipitation onto sandy soil (Fig. 10.11a) results in that the major portion of water reaches the aeration zone. With an increase in the saturation of this zone, manifesting itself in the growing soilmoisture content, $\bar{\theta}$, the infiltration moisture flux $\bar{\epsilon}$ rapidly increases. At the same time, it can be seen that in the process of shallow sediment saturation, when $\bar{\theta}$ reaches the values of the order of 0.6, water appears on soil surface and small surface runoff can be observed ($\bar{r} \approx 0.005$ day $^{-1}$); however, its rate is far below the infiltration recharge rate $\bar{\epsilon}$. It can be easily seen that $\bar{\theta}$ tends to a stationary asymptotics $\bar{\theta} = 0.70$, which also stabilizes the values of $\bar{\epsilon}$ and $\bar{r}$, with $\bar{\epsilon} + \bar{r} = \bar{P}_1$. The cessation of the intense-precipitation period results in almost complete cessation of surface runoff. Unlike this phenomenon, the gravity flow of water is very slow; such hysteresis is largely due to the essentially nonlinear character of van Genuchten's retention function (2.7), with, evidently, $\bar{\epsilon} \rightarrow \bar{P}_2$.

As it could be expected, opposite tendencies manifest themselves in precipitation falling onto loamy soil (Fig. 10.11b). The very first portions of atmospheric moisture reaching the land surface cause the formation of active surface runoff, whose rate, $\bar{r}$, can be as large as 75% of the total precipitation rate. The infiltration component $\bar{\epsilon}$

responds to changes in the moisture regime in the aeration zone with a considerable delay (5 days after the beginning of a rain event, the values of $\bar{\varepsilon}$ reach only a few percent of $\bar{P}_1$). However, the function of groundwater infiltration recharge $\bar{\varepsilon}$ increases rapidly and, in the course of stabilization of moisture regime, reaches 20% of $\bar{P}_1$. The rest 80% account for surface runoff. At the same time, upon the completion of the period of intense precipitation, the water accumulated in the aeration zone forms a stable and slightly varying infiltration flow, which tends to $\bar{\varepsilon} = \bar{P}_2$. No surface runoff is recorded in such period, $\bar{r} = 0$.

10.8.4.2 Synthesized Example 2

Multistage variations in the input function P also lead to rather interesting results (Fig. 10.12). Here we consider the conditions of precipitation falling onto covering deposits, represented mostly by clay sediments, with the initial saturation close to the limiting value. Of greatest interest are the specific features of behavior of the surface runoff function ($\bar{r}$, Fig. 10.12a): during short-time, intense rain events, moisture has no time to imbibe into soil and flows over its surface, actively forming surface runoff; during relatively weak rain events ($\bar{P} < 0.005 \text{ day}^{-1}$) water will not accumulate on land surface.

The total (cumulative) dimensionless runoff, $\bar{r}_t$, of water layer on land surface that formed within the 3-month period under consideration reaches 0.261, which accounts for more than 50% of the total precipitation depth for this period ($\bar{P}_t = 0.464$). Unlike the runoff curve, $\bar{r}$, function $\bar{\varepsilon}$ is very smooth because of the buffer effect of the aeration zone. In this case, the depth of the water layer spent for infiltration $\bar{\varepsilon}_t$ is estimated at 0.190, i.e., accounts for about 40% of $\bar{P}_t$.

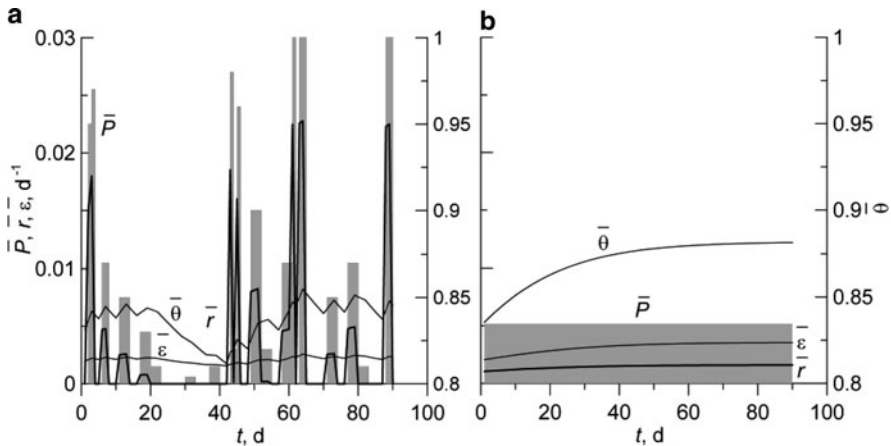


Fig. 10.12 Variations in the flow characteristics, $\bar{r}$ and $\bar{\varepsilon}$, and the relative moisture content, $\bar{\theta}$, at (a) heterogeneous and (b) homogeneous character of function $\bar{P}(t)$. In the calculations it is assumed: $k_s (= S_{\max}) = 0.05 \text{ m/day}$, $n = 1.43$, $m_a = 3.33 \text{ m}$, $\theta_r = 0.1$, $\theta_s = 0.4$, $\theta_0 = 0.35$

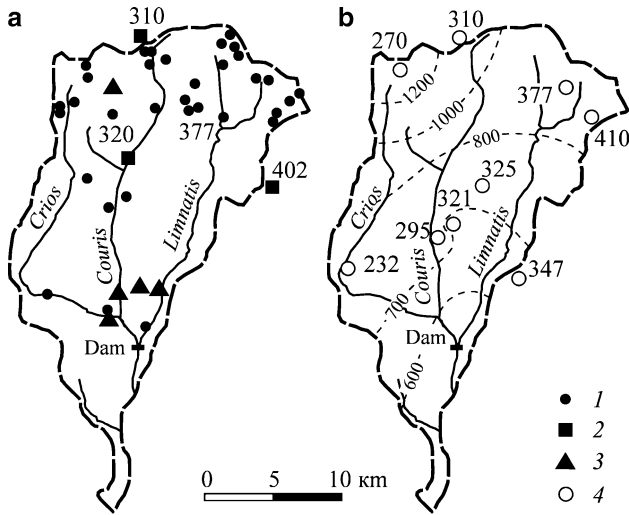


Fig. 10.13 (a) Drainage basins of the Kouris, Krios, and Limnatis rivers and (b) the area distribution of mean annual precipitation, mm (Boronina et al. 2003). (1) Spring discharge zones; (2) climatological stations where observations of potential evaporation were carried out; (3) gaging stations on rivers; (4) weather stations

The significance of the processes of atmospheric water partitioning can be seen from Fig. 10.12b. The figure gives the results of calculations carried out for precipitation averaged over 3-month period $\bar{P} = \bar{P}_t / (3 \times 30) = 0.00516 \text{ day}^{-1}$. In this case, the dimensionless depth of the surface runoff layer $\bar{r}_t$ is 0.132 (i.e., half the values obtained for synthesized variable $\bar{P}$), while that for groundwater runoff, $\bar{e}_r$, is 0.285.

10.8.4.3 Case Study Example 3

River Kouris catchment (Fig. 10.13) within the domain with the same name in the southern Cyprus has a watershed area of about 100 km^2 (Boronina et al. 2003). The flow of the river, along with the flows of two other rivers (Krios and Limnatis) running in nearby sub-basins, form the main source of water supply to the reservoir in the lower reaches of those rivers (Fig. 10.13).

A typical feature of semiarid climate is the strong time variability of atmospheric precipitation (Fig. 10.14a), reflecting itself in appropriate variations in river runoff (Fig. 10.14b): river water flow in periods of storm rainfall reaches $5\text{--}8 \text{ m}^3 \text{ s}^{-1}$, while in dry periods, it falls to tenths or hundredths of cubic meter per second. The drying up of rivers in individual periods is due to both climatic factors and water withdrawal for agriculture.

The plot of daily potential evaporation ε_{PE} (Fig. 10.15) has distinct sinusoidal character, caused by seasonal variations in climatic factors. Since the evaporation is maximal in the warm, dry season, the function ε_{PE} is in phase opposition to

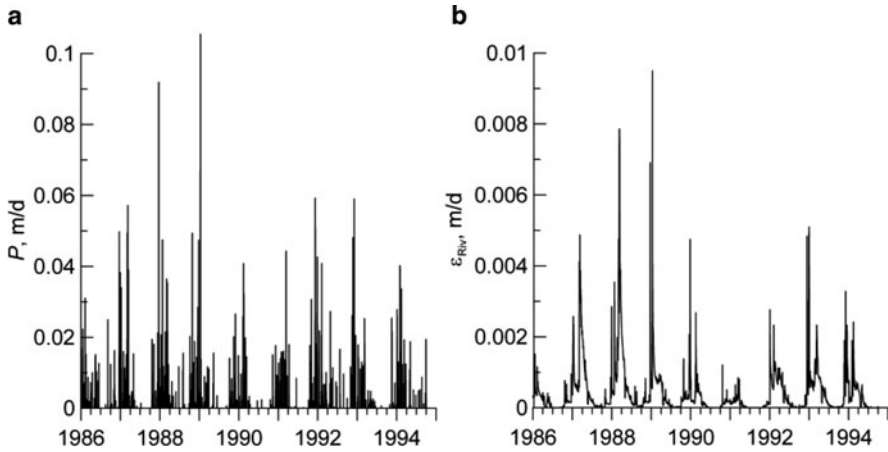
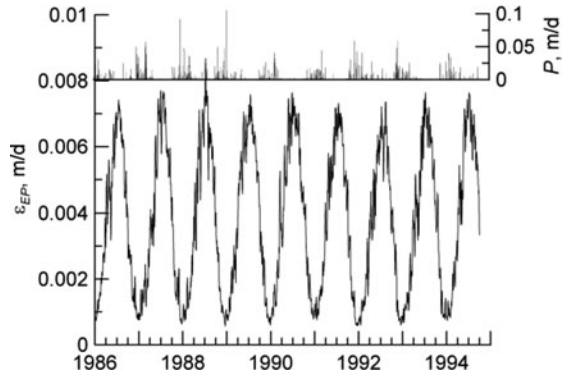


Fig. 10.14 Time series (daily measurements) of (a) precipitation (averaged over five weather stations: 295, 310, 321, 325, 320, see Fig. 10.13); (b) river runoff depth in river section before reservoir dam

Fig. 10.15 Potential evaporation (daily measurements) in many-year time intervals (weather station 320 – Fig. 10.13). The plot is combined with a plot of atmospheric precipitation



function P . This means that the moisture accumulated in the soil in periods with intense rainfall is spent for evaporation and transpiration mostly in dry seasons. Evapotranspiration entered the model (10.48) as a source function in accordance with the linear Eq. 10.47.

The target functions for the choice of parameters were taken to be the available variations in the water flow of the Kuoris River in 1986–1994, $\epsilon_{Riv}(t)$ (Fig. 10.14b), as well as the curves of accumulated flow $\sum \epsilon_{Riv} = \int_{1986}^{1994} \epsilon_{Riv}(t) dt$ (Fig. 10.17). The aim of calculations is to separate the subsurface and surface components of river runoff.

The quality of problem solution can be estimated by plots given in Figs. 10.16 and 10.17; the values of parameters at which the agreement was attained are given in figure captions. Analysis of the obtained results suggests that the physical concepts taken as the basis of the model are in agreement with the observed regularities in

Fig. 10.16 Comparison of model and actual river flow curves (daily based, 1986–1989). Model parameters:
 $k_s = S_{\max} = 0.15$ m/day,
 $n = 1.72$, $\theta_r = 0.1$, $\theta_s = 0.43$,
 $\theta_0 = 0.2$, $m_a = 3$ m,
 $E_d = 0.17 \text{ d}^{-1}$

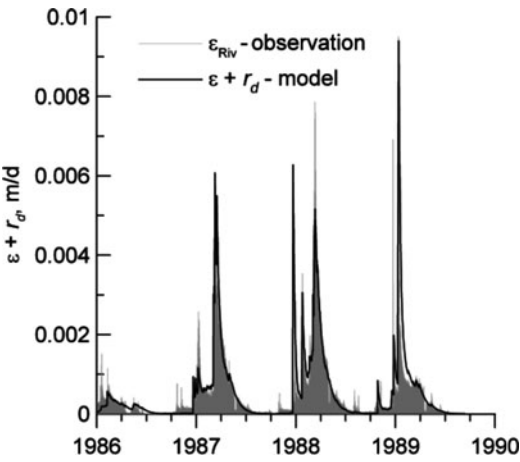
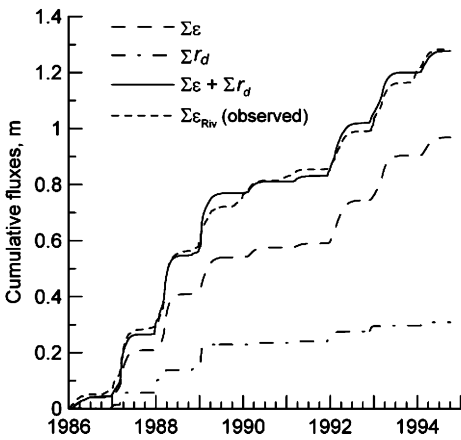


Fig. 10.17 Cumulative curves for model functions ϵ , r_d , $\epsilon + r_d$ and the recorded (*observed*) cumulative river flow

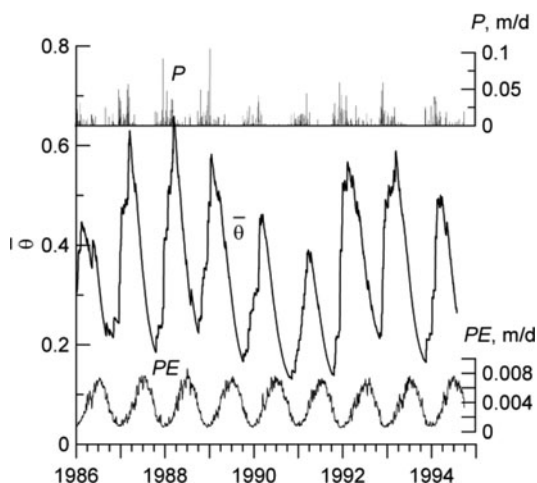


river runoff formation in the basin. The curves of daily runoff (Fig. 10.16) practically coincide, except for individual peaks associated with high floods. Analysis Model data clearly shows that peak (flood) river flow rates are mostly due to surface runoff. The total water balance of the basin, estimated by modeling, is in almost complete agreement with observational data on total river runoff (Fig. 10.17).

Model data give an insight into the contribution of evapotranspiration to the process of moisture removal from the system: evapotranspiration accounts for about 75% of total atmospheric precipitation. The rest 25% of water form surface and subsurface runoff (Fig. 10.17), and the partitioning of flows demonstrates the following proportions: 24% is surface runoff, and 76% is groundwater runoff, i.e., the mean annual infiltration recharge of groundwater amounts to 19% of the total precipitation.

Figure 10.18 gives curves illustrating the dynamics of variations in the moisture content of active soil layer. As should be expected, the relative moisture content

Fig. 10.18 Time variations in the relative moisture content of soil, $\bar{\theta}$, combined with plots of $P(t)$ and $PE(t)$



variations are sinusoidal, following seasonal rhythms. The variation range of relative moisture content ($\bar{\theta}$) is relatively wide: from 0.15 to 0.65, corresponding to the range of absolute weight percents (15–31%). It is worth mentioning that the minimal and maximal values of moisture content are somewhat shifted relative to appropriate extremums on the plots of atmospheric precipitation and potential evapotranspiration, because of inertia in the soil system.

Further we will focus on modeling of temporal variations of stable isotopes in Kouris River drainage area. As before, we neglect the possible spatial variations in the covering deposit properties, thus excluding the formation of prevailing solute migration paths. It can be readily shown that, with the average infiltration velocity and the average sediment moisture content, the characteristic migration times through the aeration zone will be of the order of several years. Therefore, it is of interest to “reconstruct” the function $C(t)$ for describing variations in natural isotope concentrations that have taken place long before the period under study (1986–1994). For this purpose, observation series for D and ^{18}O with a frequency of 1 month^{-1} recorded at a station near Gibraltar (1961–1997rr.) were used; the concentrations of stable isotopes were converted to SMOW standard.

Since the further analysis should operate with daily measurements of precipitation and the concentrations of isotopes, we suppose that the daily concentrations remained constant during a month and corresponded to the known monthly values from the database. The resulting curve for deuterium, which has a distinct sinusoidal character, is given in Fig. 10.19; it was constructed based on 13,505 values of D concentrations.

Calculations by formula (10.50) (in our case, $\theta = 0.1 + 0.33\bar{\theta}$, see Fig. 10.18) allowed us to construct the response curve given in Fig. 10.20 under the assumption that from 1961 to 1985 and from 1995 to 1997, the cyclic behavior of precipitation was the same as during the observations. It can be readily seen that the obtained

Fig. 10.19 Deuterium time series concentration in atmospheric precipitation (monthly based) for model input data

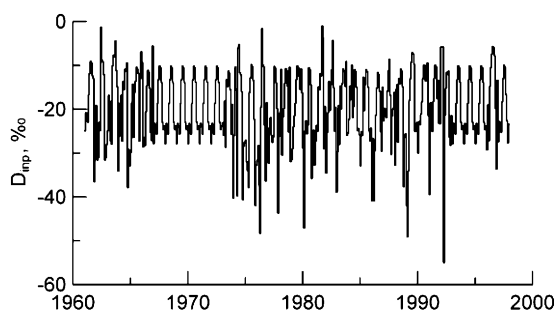
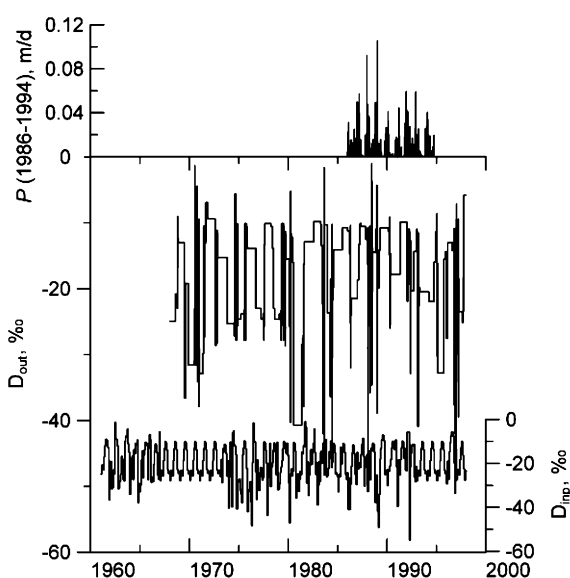


Fig. 10.20 Breakthrough concentration function, D_{out} , combined with plots of atmospheric precipitation (1986–1994) and its deuterium content, D_{inp}



distribution essentially differs from the input function: the concentration distribution becomes very heterogeneous because of contraction or extension of individual segments of the input sinusoid.

The established fact makes it problematic to use seasonal variations in groundwater isotopic composition for quantitative hydrodynamic interpretations. However, we will give the variation curves of deuterium concentration in the water that forms as a mixture of two flows – the surface and the subsurface; the latter flow is associated with an aquifer which is recharged by water infiltrating through the aeration zone; the calculations were carried out for two values of the storage capacity parameter $m\phi$ (Fig. 10.21). The obtained curves feature high, narrow peaks, associated with the formation of surface runoff during short, intensive rainfall events.

The average concentrations were calculated as the means weighted over specific discharges (runoff depths): $C_{av} = (C_1r + C_2\varepsilon)/(r + \varepsilon)$, where functions r and ε are

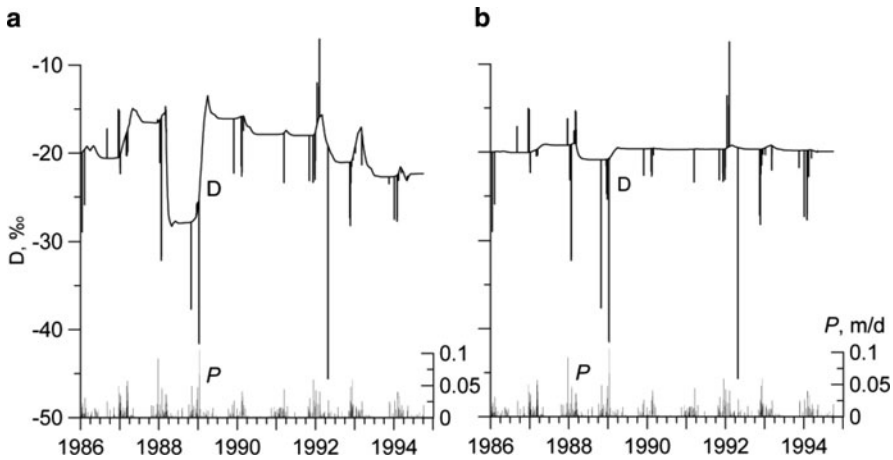


Fig. 10.21 Mean deuterium concentration resulting from mixing of two flows formed by surface and subsurface runoff. (a) $m\phi = 0.1$ m; (b) $m\phi = 1.0$ m

obtained by solving the problem of precipitation partitioning. Formula (10.35) was used to evaluate C_2 (isotope concentration in the aquifer), here $\sigma\epsilon_2^* = \epsilon/m\phi$, $C_1 = D_{\text{out}}$ (isotope concentration in the infiltration water); $C_r \equiv D_{\text{in}}$ (Fig. 10.20).

Thus, current measurements of the concentration function often give an insight into the character of the input infiltration and concentration signals that have existed long ago. This suggests the existence of a “hydrochemical memory” in the hydrodynamic systems under study (Kirchner et al. 2000).

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Chapter 11

Unsteady-State Hydrogeological Model of Evaporation-Induced Sedimentation in a Surface Reservoir

As shown in a number of publications of fundamental character (Sonnenfeld 1984; Wood and Sanford 1990; Wood 2002; Ingebritsen et al. 2006; Kohfahl et al. 2008), the major processes determining the degree of concentration of natural solutions in isolated water areas (such as lagoons or continental lakes) include evaporation from water surface and the inflow of seawater and river water. Natural groundwater systems also often play an important role in the hydrological balance of surface water bodies such as lagoons or lakes (Fujinawa et al. 2009). Such processes result in the formation of thick strata of salt deposits (evaporates). However, the studies of evaporative sedimentation basins focus mostly on the equilibrium stage of the process; they often involve some simplifying assumptions, for example, the evaporation rate from the water surface may be assumed constant (the dependence of evaporation rate from salt concentration in the solution is not taken into account), which is only true in a certain range of water mineralization values.

In this chapter, we attempt to construct a sufficiently general model taking into account the nonsteady state of salt concentration in the liquid phase of surface basins interacting with groundwater. In this case, the initial physicomathematical formulation of the problem is proposed to take into account salt crystallization, which has a specific effect on the water and salt balance of the basin.

11.1 Problem Formulation

Suppose that water evaporates from the surface of an open basin (a lagoon or a lake) (Fig. 11.1) with a rate measurably larger than that of precipitation. Initially, water level in the basin corresponds to the level in an adjacent water body, which hydraulically interacts with the basin ($h = h_0$) and contains a much greater water volume, such that $h_0 = \text{const}$. Such situation is typical, in particular, of many sea lagoons and small (“daughter”) lakes that have lost (for some geological reasons) the surface (hydrological) interaction with a “parent” lake. At the same time, the model under consideration is also valid for the conditions of discharge into the lake of subsoil water that is fed by infiltration water of a drainage basin with the equality $h = h_0$ near its water-divide line.

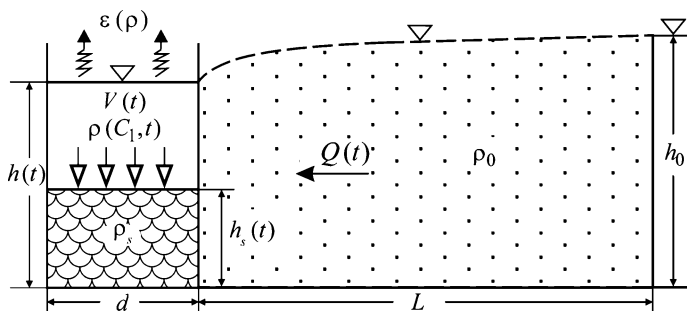


Fig. 11.1 Conceptual diagram illustrating major components of flow and mass balance of a surface reservoir connected to groundwater

Water level in the basin drops because of evaporation from the water surface, i.e., $h = h(t)$. The result is that the specific discharge of the feeding groundwater flow $Q = Q(t)$ [L^2T^{-1}] starts increasing and, accordingly, the input of salts into the basin is increasing as well. The process of salt concentration in the basin due to evaporation and the input of dissolved matter by subsoil water flow results in that the rate of evaporation, ϵ , drops, since $\epsilon = \epsilon(t)$ is generally a decreasing function.

The dependence of evaporation on salt concentration in solution C_1 has been studied in several papers, where it is shown experimentally that the dependence $\epsilon(C_1)$ becomes significant when the mineralization of solution exceeds 2–3%. [Sonnenfeld \(1984\)](#) notes that with an increase in salt concentration by 1%, the evaporativity of solution drops by about 1%. As the eutonic point is approached the evaporativity of solution decreases to 11% of that of distilled water.

The problem formulation should also include the process of salt precipitation (crystallization) from solution, which restricts the limiting concentration of dissolved salt. This process leads both to a decrease in the effective storage capacity of the water body due to the formation of a solid salt layer on its bed with a thickness of $h_s = h_s(t)$ (Fig. 11.1) and to changes in the effective cross-section area through which groundwater discharge into the water body takes place.

The behavior of the system within long periods is not quite clear, because the equilibrium of the system does not necessarily imply that the discharge rate of the solvent (water) in the composition of the feeding subsurface solution is equal to the rate of water evaporation from basin surface: the constant input of salt into the lake and the formation of a bed of precipitating salt result in the complex character of variations in the functions ρ and h_s , which determine the volume of solution in the lake and, accordingly, the value of $h(t)$. Therefore, the statement “groundwater inflows in the volume required for evaporation to be compensated for” ([Sonnenfeld 1984](#)) is not always valid.

First of all, we must specify the liquid density, ρ , as function of the concentration, C_1 . For most miscible fluid pairs, a linear density–concentration relation represents a good approximation. Hence, we employ

$$\rho = \rho^0 + \lambda C_1; \quad (11.1a)$$

here, ρ^0 is water density, $\lambda = d\rho/dC_1$ is a linear coefficient ($\lambda \approx 0.7$); the dimensions of C_1 and ρ are $[\text{ML}^{-3}]$.

Additionally, we write:

$$\rho = C_1 + C_2, \quad (11.1b)$$

where C_2 is solvent (water) concentration.

Finally, we assume that the specific evaporation rate, ε , is proportional to the molar fraction of the solvent or, in an approximate formulation, to the weight concentration

$$\varepsilon = E \left(1 - \frac{C_1}{C_1 + C_2} \right); \quad (11.2)$$

taking into account the relationship (11.1)

$$\varepsilon = E \left(1 - \frac{\rho - \rho^0}{\lambda \rho} \right); \quad (11.3)$$

here E is the specific evaporation from the surface of the freshened ($C_1 \rightarrow 0$) water $[\text{LT}^{-1}]$. In areas with arid and semiarid climate, the absolute values of E vary within the range of 2–5 m/year.

Physically, formula (11.3) is very demonstrative: the value $\eta(\rho) = (\rho - \rho^0)/\lambda \rho$ in the right part of this expression accounts for the decrease in the rate of evaporation from basin surface due to an increase in salt concentration and, accordingly, solution density ρ ; when $\rho = \rho^0$ (freshwater), $\eta(\rho) = 0$, when $\rho = 1300 \text{ kg/m}^3$ (brine), $\eta(\rho) \approx 0.4$.

11.2 Basic Balance Equation

The process under consideration can be conventionally divided into two stages: (1) the initial stage ($C_1 < C_1^*$), whose duration is determined by the time required for the saturation concentration to be attained (i.e., no salt precipitation takes place in this period), (2) the final (halogenesis) stage ($C_1 \geq C_1^*$), when the salt is precipitating from solution and starts filling the basin; hereafter C_1^* is the saturation concentration.

11.2.1 The Case of $C_1 < C_1^*$

Since the dissolved salt entering the basin with groundwater neither evaporates from its surface, nor precipitates onto its bed, we can write

$$\frac{dm_1}{dt} = bQ(t) C_{10}, \quad (11.4)$$

where $m_1 = V_1 C_1$ is the mass of dissolved salt in the basin [M]; C_{10} is salt concentration in groundwater [ML^{-3}]; $V = V(t)$ is the volume of solution in the basin [L^3], $V = Sh(t)$; S is the area of the water surface [L^2], $S = bd$, d and b are the width and length of the basin (in the direction orthogonal to the flow) [L].

The left part of the equation describes changes in the mass of dissolved solids in a closed volume; the right part is the salt mass flux that forms by the discharge rate of groundwater flow $Q(t)$. This discharge depends on the level differential between the basin $h = h(t)$ and the feeding lake h_0 . With Dupuit assumption, we have

$$Q = k (h_0^2 - h^2) / 2L, \quad (11.5)$$

where k is hydraulic conductivity [LT^{-1}], L is the distance between basins [L].

Substituting Eq. 11.5 in Eq. 11.4, we obtain:

$$\frac{d(hC_1)}{dt} = k \frac{h_0^2 - h^2}{2dL} C_{10}. \quad (11.6)$$

Equation 11.6 can be transformed, taking into account a relationship between concentrations C_1 and C_{10} with solution density ρ (11.1a):

$$\frac{d[(\rho - \rho^0)h]}{dt} = k \frac{h_0^2 - h^2}{2dL} (\rho_0 - \rho^0), \quad (11.7)$$

where ρ_0 is the density of groundwater feeding the lake.

Water balance equation for the entire mass of solution in the basin can be written as

$$\frac{dm}{dt} = qb\rho_0 - \epsilon S\rho^0, \quad (11.8)$$

where $m = V\rho$ is the total mass of matter (salt and water) in the basin. The first term in the right-hand part of Eq. 11.8 reflects the total weight flux of salt and solvent that is formed by groundwater, while the second term corresponds to the weight flux of water evaporating from the basin.

With Eqs. 11.3 and 11.5 for volumetric fluxes taken into account, Eq. 11.8 becomes

$$\frac{d(\rho h)}{dt} = k \frac{h_0^2 - h^2}{2dL} \rho_0 - E \left(1 - \frac{\rho - \rho^0}{\lambda \rho} \right) \rho^0. \quad (11.9)$$

Equations (11.7) and (11.9) can be readily transformed into dimensionless form, convenient for farther analysis; they form a system of equations, describing variations in the thickness of water layer and water density in the water body:

$$(\bar{\rho} - 1) \frac{d\bar{h}}{d\bar{t}} + \bar{h} \frac{d\bar{\rho}}{d\bar{t}} = \bar{\alpha} (\bar{\rho}_0 - 1) (1 - \bar{h}^2), \quad (11.10a)$$

$$\bar{h} \frac{d\bar{\rho}}{d\bar{t}} + \bar{\rho} \frac{d\bar{h}}{d\bar{t}} = \bar{\alpha} \bar{\rho}_0 (1 - \bar{h}^2) - \left(1 - \frac{\bar{\rho} - 1}{\lambda \bar{\rho}} \right), \quad (11.10b)$$

where

$$\bar{h} = \bar{h}/h_0, \quad \bar{\rho} = \bar{\rho}/\rho^0, \quad \bar{\rho}_0 = \rho_0/\rho^0, \quad \bar{\alpha} = \alpha h_0/E \left(\alpha = \frac{k h_0}{2dL} \right), \quad \bar{E} = E/h_0, \quad \bar{t} = \bar{E} t.$$

Or, after some additional transformations,

$$(\bar{\rho} - 1) \frac{d\bar{h}}{d\bar{t}} + \bar{h} \frac{d\bar{\rho}}{d\bar{t}} = \bar{\alpha} (\bar{\rho}_0 - 1) (1 - \bar{h}^2), \quad (11.11a)$$

$$\frac{d\bar{h}}{d\bar{t}} = \bar{\alpha} (1 - \bar{h}^2) - \left(1 - \frac{\bar{\rho} - 1}{\lambda \bar{\rho}} \right). \quad (11.11b)$$

The initial conditions are as follows:

$$\bar{h}(0) = 1, \quad \bar{\rho}(0) = \bar{\rho}_0^i. \quad (11.11c)$$

In the further analysis, we assume that the initial density of solution in the lake and groundwater density are equal, i.e., $\bar{\rho}(0) = \bar{\rho}_0$.

11.2.2 The Case of $C_I \geq C_I^*$

The formation of the bottom layer of solid salt changes the character of dependence between mass components in the balance formulas (11.4) and (11.8):

$$m_1 = V_1 C_1 + V_s \rho_s \quad (11.12)$$

– the total mass of salt in the water body;

$$m = V_1 \rho + V_s \rho_s \quad (11.13)$$

– the total mass of the matter in the water body.

Here ρ_s is salt density; $V_1 = S(h - h_s)$ is solution volume; $V_s = S h_s$ is the volume of solid salt; h_s salt layer thickness.

The formation of an impermeable salt layer on the bed of the basin deforms the vertical structure of unconfined groundwater flow. The expression for the groundwater flow rate, which tends to decrease with increasing thickness of the salt layer, can be written in the following approximate form:

$$Q \approx k \frac{(h - h_s)}{2hL} (h_0^2 - h^2). \quad (11.14)$$

Simple transformations, similar to those made before, yield the following system of dimensionless equations:

$$(\bar{\rho} - 1) \left(\frac{d\bar{h}}{d\bar{t}} - \frac{d\bar{h}_s}{d\bar{t}} \right) + (\bar{h} - \bar{h}_s) \frac{d\bar{\rho}}{d\bar{t}} + \lambda \bar{\rho}_s \frac{d\bar{h}_s}{d\bar{t}} = \bar{\alpha} (\bar{\rho}_0 - 1) \frac{\bar{h} - \bar{h}_s}{\bar{h}} (1 - \bar{h}^2), \quad (11.15a)$$

$$\frac{d\bar{h}}{d\bar{t}} - \frac{d\bar{h}_s}{d\bar{t}} + (1 - \lambda) \bar{\rho}_s \frac{d\bar{h}_s}{d\bar{t}} = \bar{\alpha} \frac{\bar{h} - \bar{h}_s}{\bar{h}} (1 - \bar{h}^2) - \left(1 - \frac{\bar{\rho} - 1}{\lambda \bar{\rho}} \right), \quad (11.15b)$$

where $\bar{h}_s = \frac{h_s}{h_0}$, $\bar{\rho}_s = \frac{\rho_s}{\rho_0^*}$.

The system of equations should be completed by an equation describing salt precipitation kinetics:

$$\rho_s \frac{dh_s}{dt} = \beta (C_1 - C_1^*), \quad (11.15c)$$

where β is a kinetic constant; in the dimensionless form:

$$\lambda \bar{\rho}_s \frac{d\bar{h}_s}{d\bar{t}} = \bar{\beta} (\bar{\rho} - \bar{\rho}^*), \quad (11.15d)$$

$\bar{\beta} = \frac{\beta}{E}$, $\bar{\rho}^* = \frac{\rho^*}{\rho_0^*}$, ρ^* is the density of solution with concentration C_1^* . With $\bar{\beta} = 0$, the system of Eq. 11.15 degenerates into the form of Eq. 11.11.

The initial conditions are as follows:

$$\bar{h}(0) = \bar{h}(\bar{\rho}_0^*), \quad \bar{h}_s(0) = 0, \quad \bar{\rho}(0) = \bar{\rho}_0^*. \quad (11.15e)$$

The dynamic hydrological models (11.11) and (11.15) are lumped-parameter models with coefficients having real physical meaning. An important feature of these models is that the surface water bodies can interact dynamically with groundwater, accumulating salts.

11.3 Numerical Solutions of the Problem and Their Analysis

Solutions of the system of Eqs. 11.11 and 11.15 can be obtained in a closed analytical form only with some simplifying assumptions. To better analyze the process, it is reasonable to solve these systems by a numerical (finite-difference) method. Specific solutions $\bar{h}(t)$, $\bar{h}_s(t)$, and $\bar{\rho}(t)$, obtained by the classic Euler method are plotted in Figs. 11.2–11.4. The character of plots suggests the following tendencies in the development of the process.

1. Water evaporation causes a drop in solution level in the basin (Fig. 11.2). The rate of level drop is the greater, the less is the value of the constant $\bar{\alpha}$, characterizing the ratio between the rates of groundwater inflow into the basin and evaporation from it. When $\bar{\alpha} < 0.1$ –0.5 (in the accepted range of $\bar{\rho}_0$ values, $\bar{\rho}_0 \leq 1.03$), the basin will dry up completely ($\bar{h} < 0.1$). When $\bar{\alpha} > 0.1$ –0.5, concentrated solution will accumulate in the basin in appreciable volumes.

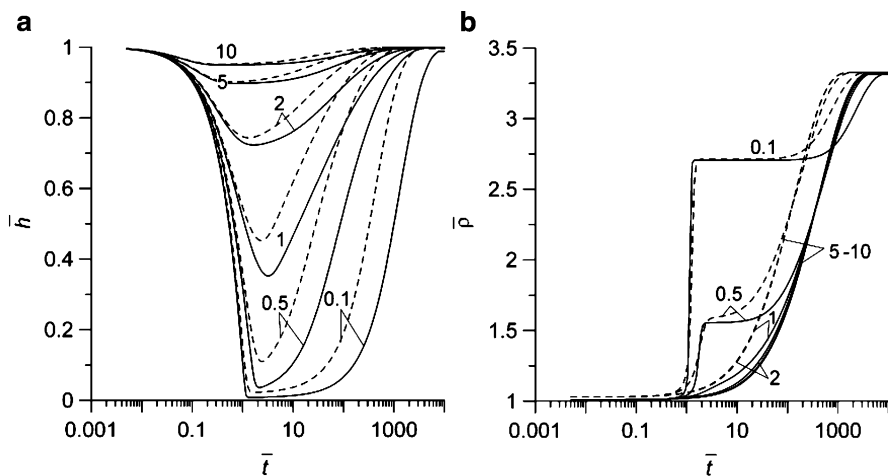
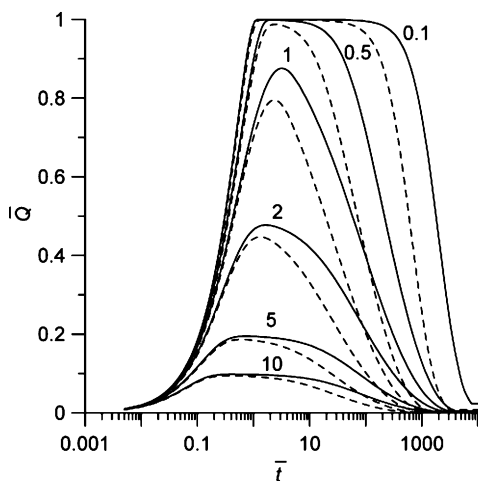


Fig. 11.2 Functions (a) $\bar{h} = f(\bar{t})$ and (b) $\bar{\rho} = f(\bar{t})$, plotted for the case $\bar{\beta} = 0$, i.e., no salt precipitation from solution. The figures at curves are the values of $\bar{\alpha}$. Full lines are for $\bar{\rho}_0 = 1.01$, dashed lines are for $\bar{\rho}_0 = 1.03$

Fig. 11.3 Plot of function $\bar{Q}(\bar{t})$. The figures at curves are the values of $\bar{\alpha}$. The full lines are for $\bar{\rho}_0 = 1.01$, the dashed lines are for $\bar{\rho}_0 = 1.03$



Clearly, it is reasonable to restrict the analysis of behavior of the system to the case $\bar{\alpha} > 1.0$, which is of greatest practical interest. With lesser $\bar{\alpha}$, especially $\bar{\alpha} < 0.5$, the solution will rapidly concentrate in a thin bottom layer of the basin. As can be seen, in the examined variation range of parameter $\bar{\alpha}$, function $\bar{h}(\bar{t})$ has an extreme character: a period of decline in the values of $\bar{h}(\bar{t})$ changes to a period of its growth (minimums with $d\bar{h}/d\bar{t} = 0$ can be seen in all plots). This type of behavior of the system can be explained by a decline in the evaporation rate from the water surface with an increase in salt concentration in the basin (see formula (11.3)). The sign of gradient, dQ/dt , of the flow of groundwater

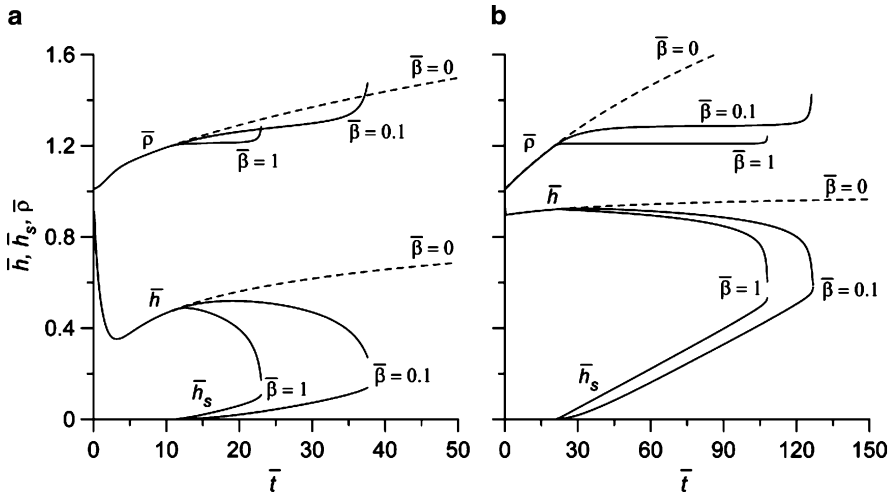


Fig. 11.4 Functions $\bar{h} = f(\bar{t})$, $\bar{h}_s = f(\bar{t})$, and $\bar{\rho} = f(\bar{t})$, characterizing the process of evaporative concentration of solution, accompanying the precipitation of salts at different values of parameter (a) α : 1.0 and (b) 5.0. The calculations are made with $\bar{\rho}_0 = 1.01$, $\bar{\rho}^* = 1.2$, and $\bar{\rho}_s = 1.2$. Dashes show the curves calculated with salt crystallization not taken into account

changes accordingly in the extreme point, as can be seen from the character of plot (Fig. 11.3) of the dimensionless function

$$\bar{Q}(\bar{t}) = \frac{Q}{dE} = \alpha \left[1 - \bar{h}^2(\bar{t}) \right]. \quad (11.16)$$

From the comparison of plots constructed at $\bar{\rho}_0 = 1.01$ and 1.03, it follows that the minimums of the function $\bar{h}(\bar{t})$ are the greater, the greater is water mineralization.

The rate of density increase in the basin is also determined by the ratio between parameters E and α , which control the rate of water evaporation and groundwater flow discharge, as well as by the initial density of solutions, $\bar{\rho}_0$. The greater groundwater inflow into the basin, the slower the density (mineralization) growth.

The presented plots (Fig. 11.2, a) allow the solution concentration to increase to unrealistically high density values ($\bar{\rho}(t) > 1.4$ –1.5), which is an artefact resulting from the neglect of salt precipitation in calculations.

2. The more complete model leads to an even more complex character of the theoretical curves $\bar{h}(t)$ and $\bar{\rho}(t)$ (Fig. 11.4). Thus, the function describing solution level variations in the basin has already two extremums. The second is due to changes (a decrease) in the volume of solution caused by the removal from the liquid phase of salt, whose density $\bar{\rho}_s$ is much greater than solution density in the eutonic point $\bar{\rho} = \bar{\rho}^*$. Further, it can be seen that after the saturation concentration is attained, the rate of variations in solution density becomes dependent on the precipitation rate constant. When its values are large enough (in our case,

$\bar{\beta} = 1.0$), the density $\bar{\rho}$ remains almost unchanged. When the values of $\bar{\beta}$ are small ($= 0.1$) the solution is oversaturated. The character of function $\bar{h}(t)$ and the accumulation rate of solid salts also depends on parameter $\bar{\beta}$. Overall, the process features a nearly linear increase in the thickness of the salt layer $\bar{h}_s(t)$ on the basin bed, and the functions $\bar{h}(t)$ and $\bar{h}_s(t)$ tend to the same value. At the moment when $\bar{h} = \bar{h}_s$, the basin becomes completely dry and filled with salt.

The main conclusions are as follows. The proposed model proves the need to jointly analyze the process of groundwater flow and the water-salt balance for the basin in the analysis of evaporative sedimentation conditions. In particular, to take into account the nonsteady phase of the process is a necessary element of this type of analysis in the calculation of the amount of salt accumulated in the basin in the process of evaporative saturation of solution. It is shown that appreciable amounts of salt can form in the basin only if salt is permanently supplied from adjacent areas, in this case, by groundwater. The concentrations of dissolved salts in groundwater can however be low. The proposed approach can be of use in calculating the nonsteady regime of subsoil aquifers with water evaporating from their surface, as well as in studying isotope fractionation in surface and subsurface waters during their evaporation. Finally, the equations proposed here can be generalized to multicomponent solutions, the progress that may allow several stages of evaporative sedimentation to be described in a nonsteady formulation.

At the same time, the model considered here is, clearly, very idealized. In particular, it does not take into account the actual hydrodynamic conditions of interaction between the flows of fresh water and brines accumulating in the basin. This interaction manifests itself, primarily, in the formation of convection cells under the surface basin bottom (Kohfahl et al. 2008; Fujinawa et al. 2009). Because evaporation concentrates the salt lake water, the brine, driven by density forces, may flow into the fresher groundwater, and cellular flow circulation may occur below the salt lake bottom. Recycling brines are carried back up toward the lake by the fresher flow. This process has to be described in the framework of other type of hydrogeological models that will be analyzed in the next part of this work.

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Part V

Variable-Density Flow and Solute Transport: Physical Phenomena and Mathematical Formulation

The description of the solute migration processes considered above was based on the assumption that the physical properties (the density, ρ , and viscosity, μ) of formation water and solutions or liquids entering the aquifer from the surface are identical. Also, possible variations in these properties under natural conditions, corresponding to heterogeneous initial conditions, were neglected. The need for the development of more accurate hydrogeological models that consider the effects caused by the spatial and temporal variations in water density and viscosity across the flow field continues to increase due to a large number of environmental problems such as saltwater intrusion in exploited coastal aquifers; leakage from a surface reservoir, accumulating dense waste; disposal of radioactive or toxic waste in deep geological formations; geological sequestration of carbon dioxide; and exploitation of groundwater systems exhibiting vertical stratification of water quality (in particular, in regions containing saline disposal basins).

The behavior of a hydrodynamic system as a response to the appearance in it of a mobile liquid, whose physical properties differ from those of groundwater, will be considered below from several complementary viewpoints. First, we will consider the main laws determining the equilibrium and dynamics of freshwater–saltwater interface between the liquids differencing in density. Next, we will assess the role of dispersion phenomena and the heterogeneity of rock hydraulic properties, leading to diffusion of the fronts of mixing different-density solutions and making their forms more complex. Here, analytical solutions are supplemented by numerical modeling of migration processes, allowing a combination of their different mechanisms to be examined. In conclusion, we will give individual examples of studying groundwater pollution by dense brines at concrete sites of hydrogeological studies. In this case, mathematical modeling is among the main tools used to study and forecast groundwater salinization processes.

Chapter 12

Dynamic Equilibrium of Freshwater–Saltwater Interface

In this chapter, idealized groundwater flow systems containing two liquids, namely freshwater and saltwater, of different density separated by an abrupt interface are considered under steady-state conditions. Classical approaches to the determination of the shape of the interface at equilibrium related to the two benchmark problems, seawater intrusion in a coastal aquifer, and saltwater upconing beneath a partially penetrating pumping well, are reviewed. In particular, it is shown that Ghyben–Herzberg approximation for Dupuit–Forchheimer-based models provide practically valuable insight into the behavior of the groundwater systems under consideration.

12.1 Basic Steady-State Models

12.1.1 Interface Between Two Immiscible Liquids in Equilibrium

Consider a fragment of two-dimensional (in the x – z plane) flow of two liquids, 1 and 2 (Fig. 12.1), separated by a sharp interface s (it is implicitly assumed that the fluids are *immiscible*). The flows in both domains occupied by liquids with different densities are governed by the gradients of hydrostatic heads (h_1 and h_2) and described by Darcy law:

$$\begin{aligned} \mathbf{q}_1 &= -k_1 \nabla h_1, \\ \mathbf{q}_2 &= -k_2 \nabla h_2, \end{aligned} \quad (12.1)$$

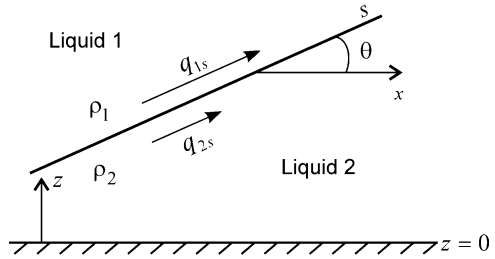
where

$$h_{1,2} = P / \rho_{1,2} g + z, \quad (12.2)$$

P is pressure [$\text{ML}^{-1}\text{T}^{-2}$], $k_{1,2}$ is hydraulic conductivity for liquids 1 and 2 [LT^{-1}], ρ_1 and ρ_2 are liquid densities [ML^{-3}], g is free-fall acceleration [LT^{-2}].

Suppose that the position of the interface between two liquids, s , is stationary. This means that it plays the role of an impermeable boundary for each mobile

Fig. 12.1 Dynamic equilibrium of the interface between two mobile liquids with different densities



liquid, such that only tangent components of Darcy velocities q_{1s} and q_{2s} exist on the surface s (Bear 1972):

$$\begin{aligned} q_{1s} &= -k_1 \frac{\partial h_1}{\partial s} = -k_1 \left(\frac{1}{\rho_1 g} \frac{\partial P}{\partial s} + \frac{\partial z}{\partial s} \right), \\ q_{2s} &= -k_2 \frac{\partial h_2}{\partial s} = -k_2 \left(\frac{1}{\rho_2 g} \frac{\partial P}{\partial s} + \frac{\partial z}{\partial s} \right). \end{aligned} \quad (12.3)$$

If we neglect the capillary effects on the interface between the liquids, the continuity equation implies that the pore-fluid pressure on the freshwater side of the interface is equal to the pressure on the saltwater side of the interface and the slopes of the freshwater and saltwater pressure distribution curves versus depth at any point s are equal. Now, eliminating the derivative $\partial P / \partial s$ from Eq. 12.3, we obtain (Bear 1972; Bear and Cheng 2010)

$$\frac{\partial z}{\partial s} = \sin \theta = \frac{q_{1s}}{k_1 \Delta \bar{\rho}_1} - \frac{q_{2s}}{k_2 \Delta \bar{\rho}_2} \equiv \frac{\mu_1 q_{1s} - \mu_2 q_{2s}}{Kg(\rho_2 - \rho_1)}, \quad (12.4)$$

where θ is the angle between the surface s and the x -axis,

$$\Delta \bar{\rho}_1 = \frac{\rho_2 - \rho_1}{\rho_1}, \quad \Delta \bar{\rho}_2 = \frac{\rho_2 - \rho_1}{\rho_2}, \quad (12.4a)$$

K is the permeability, μ_i is the dynamic viscosity.

Hubbert (1940) was among the first to examine the functional relationship (12.4) from the viewpoint of describing the equilibrium state of mobile different-density liquids having a stationary common boundary. An extended physical interpretation of this relationship and analysis of some particular cases that follow from it can be found in later publications (Todd 1959; De Wiest 1965; Walton 1970; Bear 1972; Bear and Cheng 2010).

Thus, expression (12.4) allows one to readily determine (forecast) the character of the slope of interface s . For example, if liquid 2 is immobile, i.e., $q_{2s} = 0$ (the case of greatest interest for hydrogeologists), we have

$$\frac{\partial z}{\partial s} = \sin \theta = \frac{q_{1s}}{k_1 \Delta \bar{\rho}_1}. \quad (12.5)$$

From here it follows that the motion of the lighter liquid over the surface of an immobile denser one, yields $\sin \theta > 0$, i.e., the interface rises in the direction of flow, and the slope increases with q_{1s} . Similarly, it can be shown that when $q_{1s} = 0$, $\sin \theta < 0$, i.e., the contact will feature a drop in the absolute values of z . This is true, for example, for a flow of bottom water overlain by lighter, immobile oil at oil deposits.

12.1.2 Ghyben–Herzberg Relation (Approximation)

Now, let us consider a fragment of groundwater flow with a free surface moving over an impermeable boundary formed by immovable denser water, as is the case in the domain of groundwater discharge into a sea water area (Fig. 12.2). Since the equipotential lines h_1 are normal to the interface, we can write the following expression for the tangent to the Darcy velocity

$$q_{1s} = -k_1 \frac{\partial h_1}{\partial s}. \quad (12.6)$$

If we assume that the gradients of subsoil water surface and function h_1 coincide, then, substituting (12.6) into (12.5) we obtain

$$\frac{\partial z}{\partial s} = -\frac{1}{\Delta \bar{\rho}_1} \frac{\partial h_1}{\partial s}, \quad (12.7)$$

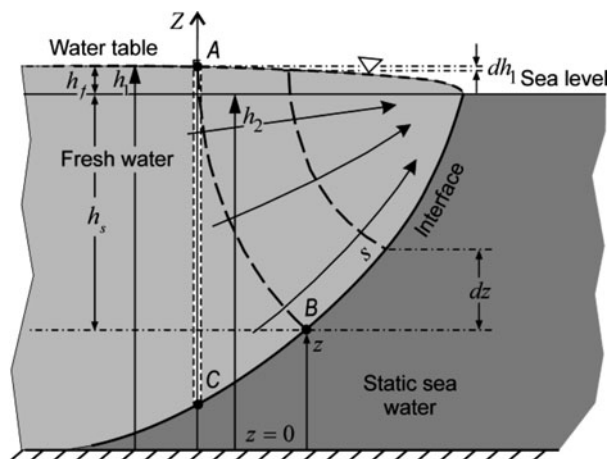


Fig. 12.2 Dynamic equilibrium of interface formed by moving fresh water overlying static sea water. s is the interface; AB is the equipotential line; AC is a conventional well, showing the position of the interface between the liquids in the level measurement points, h_1 ; h_2 is saltwater head (const)

or

$$dz = -\frac{1}{\Delta\bar{\rho}_1}dh_1, \quad (12.8)$$

which can be considered as differential forms of the representation of the well-known Ghyben–Herzberg relationship (see below).

Upon integrating the left and right parts of Eq. 12.8 from $[z, h_2]$ to $[h_1, h_2]$:

$$\int_z^{h_2} dz = -\frac{1}{\Delta\bar{\rho}_1} \int_{h_1}^{h_2} dh_1; \quad (12.9)$$

we have

$$(h_2 - z) = -\frac{1}{\Delta\bar{\rho}_1}(h_2 - h_1) = \frac{1}{\Delta\bar{\rho}_1}(h_1 - h_2), \quad (12.10)$$

or

$$h_s = \frac{1}{\Delta\bar{\rho}}h_f, \quad (12.11)$$

where $h_s = (h_2 - z)$ is the thickness of freshwater bed between the plane $z = h_2$ and the interface separating different-density waters; $h_f = (h_1 - h_2)$ is the excess of freshwater head over the denser water head; $\Delta\bar{\rho} \equiv \Delta\bar{\rho}_1$. The formula (12.11), referred to as *Ghyben–Herzberg relation (approximation)*, can be also derived from an evident hydrostatic equality:

$$\rho_2gh_s = \rho_1g(h_s + h_f). \quad (12.11a)$$

Under these hydrostatic conditions, the weight of fresh water is balanced by the weight of sea water at their interface under the aquifer. The Ghyben–Herzberg relation (12.11) can underestimate or overestimate the freshwater thickness, because it assumes no vertical head gradients and consequently no vertical flow. Estimation of the interface depth needs to consider the vertical head gradients and aquifer anisotropy that may be present.

For example, it can be seen from Fig. 12.2 that, since the equipotential line AB , originating from point A , is curvilinear, the actual depth (the vertical segment AC) to the interface exceeds the estimated value, $h_s + h_f$ (point B), corresponding to the Ghyben–Herzberg approximation (Bear 1972).

There are some other limitations referring to the application of the Ghyben–Herzberg formula and other models of the motion of immiscible fluids with a sharp interface. Such limitations are discussed in detail in several special studies. Thus, there is diffusive mixing of salt ions across the interface, which diminishes the interface, and saltwater wedge recedes (see also Sect. 11.2). The extent of mixing is a function of both freshwater flow rates and the geologic characteristics of the aquifer. Consequently a sharp interface concept is not realistic, especially when the thickness of dispersion zone is considerable (Bear 1979). The most accurate models of saltwater intrusion shall incorporate diffusion components (Chap. 14). Nevertheless, the accuracy of many calculations with formula (12.11) is quite sufficient for practical estimates.

12.2 Approximate Solutions of the Problem of the Shape of the Seawater–Fresh Groundwater Interface

In coastal areas, groundwater quality may be degraded by intrusion of salt seawater into freshwater aquifers. The difference between groundwater and seawater densities, other conditions being the same, is the main factor determining the position of their interface in coastal aquifers. The mean density of seawater, ρ_s , varies between 1,022 and 1,028 kg/m³. Viscosity differences play only a minor role in this process and can be ignored.

This class of problems has been studied well. Sufficiently rigorous steady-state solutions, taking into account, in particular, the existence of a vast zone of subaqual freshwater discharge (outflow face), have been obtained with the use of potential functions and complex variables (Henry 1959; Bear 1972; Strack 1976; Guo and Jiu 2007; Bear and Cheng 2010). Analytical and modeling description of the shape of freshwater–seawater interface in coastal aquifers exploited by pumping wells located above the interface is of heightened interest (Strack 1976; Paster and Dagan 2008a; Bear and Cheng 2010). Indeed, freshwater withdrawal by such wells results in a drop in piezometric head and as a consequence causes a local rise in interface elevations (so called *upconing* phenomenon). Under certain conditions, the rising interface may reach the pumping well; however, specially optimized water withdrawal schedule may exclude such process, allowing a large part of the freshwater flowing to the sea be intercepted and collected, without the interface rising to the well or well clusters (Bear and Cheng 2010).

A case study illustrating the discussed effects as well as field and modeling technique capability to investigate seawater intrusion into a coastal area will be presented in Chap. 16. In addition, special analysis will present major findings from the study of different stages of saltwater upconing in idealized groundwater systems having a flat initial fresh–saltwater interface (Sects. 12.3 and 14.2.3).

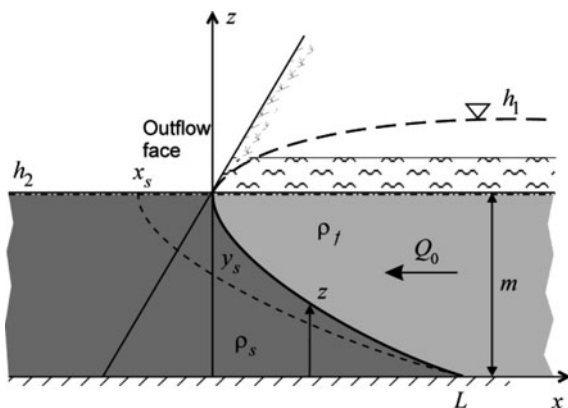
In this subsection we will focus on simplified seawater intrusion models which are based on the classical Ghyben–Herzberg relationship assuming freshwater and seawater immiscible with a well-defined interface (Ten Hoorn 1981; Van Dam and Sikkema 1982; Essink and Boekelman 2000; Essink 2001). Under steady-state conditions, the saltwater is assumed to be stationary, while the freshwater is assumed moving. Pumping wells are not considered.

12.2.1 A Confined Coastal Aquifer

Suppose that groundwater discharges into the sea at a constant specific flow rate, Q_0 (Fig. 12.3). Since the interface between freshwater and the seawater wedge is impermeable, we can write

$$Q_0 = k(m - z) \frac{dh_1}{\partial x}, \quad (12.12)$$

Fig. 12.3 Schematic diagram showing the main components controlling the location of the freshwater–seawater interface in confined aquifer (the dashed line shows the interface between the sea and fresh waters under the assumption of subaquatic discharge of the latter)



where k is hydraulic conductivity, m is aquifer thickness, $z = z(x)$ is the current coordinate of the interface; the direction of the flow is opposite to that of the x -axis; therefore, both parts of the equality (12.12) have the same sign.

In accordance with (12.8)

$$Q_0 = -k(m - z)\Delta\bar{\rho}\frac{dz}{dx}; \quad (12.13)$$

hereafter,

$$\Delta\bar{\rho} \equiv \Delta\bar{\rho}_1 = \frac{\rho_s - \rho_f}{\rho_f}, \quad (12.14)$$

ρ_s and ρ_f are the densities of the sea and fresh water, respectively. Separating variables and integrating this equation under the conditions $x = 0$, $z = m$, we finally obtain

$$(m - z)^2 = \frac{2Q_0}{k\Delta\bar{\rho}}x, \quad (12.15)$$

i.e., the interface line is a parabola. Assuming $z = 0$, one may obtain a relationship between the total freshwater discharge to the sea, Q_0 , and the length of seawater wedge intruding into the aquifer, $x = L$,

$$L = k\Delta\bar{\rho}m^2/2Q_0. \quad (12.16)$$

It is seen that the lower the specific discharge rate, Q_0 , the greater the length of seawater wedge, L , and vice versa.

Equation 12.15 can be written as

$$\bar{y}^2 - 2\bar{x}/G = 0, \quad (12.17)$$

allowing it to be compared with the solution of Glover (1959) and Henry (1959)

$$\bar{y}^2 - 2\bar{x}/G - (1/G)^2 = 0; \quad (12.18)$$

here $\bar{x} = \frac{x}{m}$, $\bar{y} = \frac{y}{m}$, $y = m - z$,

$$G = k\Delta\bar{\rho}m/Q_0. \quad (12.19)$$

The solution (12.18) was obtained in a stricter formulation, allowing the presence of a zone of subaqual discharge (outflow face) left of the point $x = 0$, $z = m$:

$$x_s/m = -1/2G, \quad (12.20)$$

where x_s is the length of outflow face (Fig. 12.3). The existence of the outflow face cannot be predicted by the Ghyben–Herzberg assumption. Accordingly, the coordinate of the intersection point of the interface and the z -axis, y_s , is determined from the relationship:

$$y_s/m = 1/G (\bar{z}_s = 1 - 1/G). \quad (12.21)$$

The dimensionless parameter G (12.19) can be regarded as a relationship determining the *balance* between the flux induced by density convection and the convection flow (Simpson and Clement 2004). When $G \ll 1$, forced convection dominates in the system, while when $G \gg 1$, the convection induced by the solution density contrast dominates. We will return to the solutions (12.17) and (12.18), as some limiting analytical “standards”, in the Sect. 14.2.1, devoted to numerical methods of studies of the appropriate migration problem of different-density solutions.

12.2.2 A Leaky Confined Coastal Aquifer

Consider the idealized leaky system as shown in Fig. 12.4. The aquifer is recharged by fresh water entering from the landward boundary and by the leakage through a semipervious confining layer from the overlying phreatic aquifer in which hydraulic head remains constant, $h = h_0$, and higher than the main aquifer piezometric head.

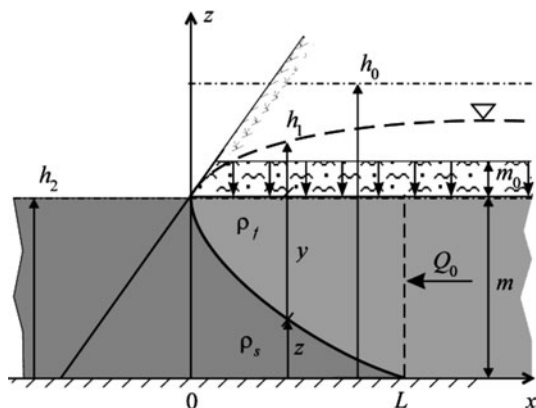


Fig. 12.4 Schematic cross-sectional view of seawater intrusion into a confined leaky aquifer

We also assume that the thickness of the main aquifer is m , its hydraulic conductivity is k , and the appropriate characteristics of the separating layer are m_0 and k_0 . The heads of the fresh and sea (salt) waters are h_1 and $h_2 = \text{const}$, respectively (Fig. 12.4).

Assume $y = m = z$. Now the equation for the freshwater discharge, $Q = Q(x)$, in accordance with Darcy law,

$$Q = ky \frac{dh_1}{dx} = Q_0 + \frac{h_0 - h_1}{c}(L - x), \quad (12.22)$$

where Q_0 is the freshwater discharge at the boundary of the saltwater wedge $x = L$ (Fig. 12.4), $c = m_0/k_0$.

Next, from (12.8) we have

$$dh_1 = -\Delta\bar{\rho} dz = \Delta\bar{\rho} dy, \quad (12.23)$$

whence, after integration from $[h_2, h_1]$ to $[0, y]$, we obtain the dependence between h_1 and y :

$$h_1 = h_2 + \Delta\bar{\rho} y. \quad (12.24)$$

Differentiating (12.22), considering the latter relationship, we come to an ordinary differential equation in function $y = y(x)$:

$$k\Delta\bar{\rho}y \frac{d^2y}{dx^2} + k\Delta\bar{\rho} \left(\frac{dy}{dx} \right)^2 + \frac{h_0 - h_2 - \Delta\bar{\rho}y}{c} = 0. \quad (12.25)$$

Let us introduce dimensionless variables and normalize the head differential ($h_0 - h_2$):

$$\bar{y} = y/m, \quad \bar{x} = x/\lambda, \quad \lambda = \sqrt{kcm} = \sqrt{kmm_0/k_0}, \quad \varepsilon = (h_0 - h_2)/\Delta\bar{\rho}m \quad (12.26)$$

(λ has the meaning of leakage parameter).

Now the Eq. 12.25 acquires the dimensionless form

$$\bar{y} \frac{d^2\bar{y}}{d\bar{x}^2} + \left(\frac{d\bar{y}}{d\bar{x}} \right)^2 - \bar{y} + \varepsilon = 0. \quad (12.27)$$

Some partial solutions for Eq. 12.25 were obtained in the work [Van Dam and Sikkema \(1982\)](#). We think it possible to obtain the general solution of Eq. 12.27 with the help of the substitution ([Ten Hoorn 1981](#))

$$\frac{d\bar{y}}{d\bar{x}} = \xi, \quad \frac{d^2\bar{y}}{d\bar{x}^2} = \frac{d\xi}{d\bar{x}} = \frac{d\xi}{d\bar{y}} \frac{d\bar{y}}{d\bar{x}} = \xi \frac{d\xi}{d\bar{y}}, \quad (12.28)$$

transforming (12.27) into

$$\bar{y}\xi \frac{d\xi}{d\bar{y}} + \xi^2 - \bar{y} + \varepsilon = 0. \quad (12.29)$$

Next, we assume $\eta = \xi^2$ to obtain finally:

$$\bar{y}\eta' + 2\eta - 2\bar{y} + 2\varepsilon = 0. \quad (12.30)$$

We have solved equations of this type (Sect. 10.3.2) with the help of the substitution $\eta = uv$:

$$u'v + u\left(v' + \frac{2}{\bar{y}}v\right) - 2 + \frac{2}{\bar{y}}\varepsilon = 0, \quad (12.31)$$

whence $v = \bar{y}^{-2}$. To find u we integrate the equation

$$u' / \bar{y}^2 - 2 + 2\varepsilon / \bar{y} = 0, \quad (12.32)$$

to obtain

$$u = 2\bar{y}^3 / 3 - \bar{y}^2 \varepsilon + C \quad (12.33)$$

(C is a constant of integration). Since $\eta = uv$,

$$\eta = \xi^2 = \left(\frac{d\bar{y}}{d\bar{x}}\right)^2 = \frac{C}{\bar{y}^2} + \frac{2}{3}\bar{y} - \varepsilon, \quad (12.34)$$

$$\frac{d\bar{y}}{d\bar{x}} = \sqrt{\frac{C}{\bar{y}^2} + \frac{2}{3}\bar{y} - \varepsilon}. \quad (12.35)$$

For the model situation in hand (Fig. 12.4), the constant C can be found from the condition

$$Q = Q_0 = k(m - z) \frac{dh_1}{dx} \Big|_{x=L}, \quad (12.36)$$

or

$$\frac{d\bar{y}}{d\bar{x}} \Big|_{\bar{y}=1} = \frac{Q_0 \lambda}{\Delta \bar{\rho} k m^2} = \sqrt{C + \frac{2}{3} - \varepsilon}. \quad (12.37)$$

Denoting $\bar{Q}_0 = Q_0 \lambda / \Delta \bar{\rho} k m^2$, we obtain

$$C = \bar{Q}_0^2 + \varepsilon - 2/3. \quad (12.38)$$

The equation for the interface between the liquids can be found by integration (12.35)

$$\int_0^{\bar{y}} \frac{\bar{y} d\bar{y}}{\sqrt{C + 2\bar{y}^3/3 - \varepsilon \bar{y}^2}} = \int_0^{\bar{x}} d\bar{x} = \bar{x}, \quad (12.39)$$

For the overwhelming majority of the practically significant situations, we have $\varepsilon \gg 2\bar{y}/3$ ($\bar{y} \leq 1$). In this case, the integral acquires a tabulated form ($-\sqrt{C - \varepsilon \bar{y}^2}/\varepsilon$) and the solution becomes simpler:

$$\sqrt{C} \left(1 - \sqrt{1 - \varepsilon \bar{y}^2 / C} \right) / \varepsilon = \bar{x}. \quad (12.40)$$

It can be easily seen that the solution is valid when the expression under the radical is positive, which is always true when $\bar{q}_0 > \sqrt{2/3}$.

When $\bar{Q}_0^2 \gg \epsilon$, i.e., the leakage can be neglected, $\sqrt{1 - \epsilon \bar{y}^2 / C} \approx 1 - \epsilon \bar{y}^2 / 2C$ and

$$\bar{y}^2 / 2\sqrt{C} = \bar{x}, \quad (12.41)$$

which exactly corresponds to expression (12.17) for confined flow in an isolated bed, obtained before.

The dimensionless length of seawater wedge can be found from the solution (12.40) with $\bar{y} = 1$ ($y = m$):

$$\bar{L} = \frac{L}{\lambda} = \frac{\sqrt{C}}{\epsilon} \left(1 - \sqrt{1 - \frac{\epsilon}{C}} \right). \quad (12.42)$$

12.2.3 A Phreatic Coastal Aquifer Under Recharge Conditions

In this case, according to (3.1), we have $Q = Q(x)$, such that

$$dQ = \epsilon dx, \text{ or } Q = Q_0 + \epsilon(L - x), \quad (12.43)$$

where ϵ is the recharge rate; Q_0 is the specific flow rate at $x = L$ (Fig. 12.5).

In accordance with Darcy law,

$$Q_0 + \epsilon(L - x) = k(h_1 - z) \frac{dh_1}{dx}. \quad (12.44)$$

Let us introduce new variables $\eta = h_1 - z$ and $\xi = L - x$. Now, in Eq. 12.44, we have $h_1 - z = \eta(1 + \Delta\bar{\rho})$, $dh_1 = -\Delta\bar{\rho}dz = \Delta\bar{\rho}d\eta$. Separating variables, we obtain

$$-(q_0 + \epsilon\xi)d\xi = k\Delta\bar{\rho}(1 + \Delta\bar{\rho})\eta d\eta, \quad (12.45)$$

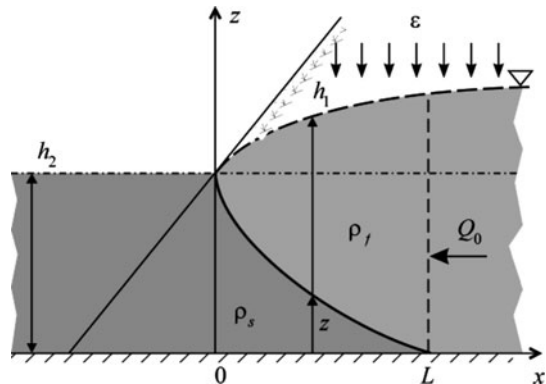


Fig. 12.5 Schematic diagram showing the seawater intrusion into an unconfined aquifer subject to area-distributed infiltration recharge

or

$$-ad\xi - bd\xi^2/2 = d\eta^2/2, \quad (12.46)$$

where $a = Q_0/k\Delta\bar{\rho}(1 + \Delta\bar{\rho})$, $b = \varepsilon/k\Delta\bar{\rho}(1 + \Delta\bar{\rho})$.

Let us integrate the left part (12.46) from $\xi = L(x = 0)$ to ξ , and the right part, from $\eta = 0$ ($z = h_2$) to η . The result is the equation for the interface:

$$(h_2 - z)^2 = 2(a + bL)x - bx^2. \quad (12.47)$$

To find the length L of the seawater wedge, we use the condition $x = L$ at $z = 0$. Solving the appropriate algebraic equation yields (Bear and Cheng 2010)

$$L = \frac{Q_0}{\varepsilon} \left(\sqrt{1 + \frac{h_2^2 \varepsilon}{Q_0^2} k \Delta\bar{\rho} (1 + \Delta\bar{\rho})} - 1 \right). \quad (12.48)$$

Suppose that the flow domain in the right part of Fig. 12.5 is limited by an impermeable boundary at a distance $x = L_1$. Now $Q_0 = (L_1 - L)\varepsilon$, and the Eq. 12.48 becomes

$$L_1 - L = x_t = \sqrt{L_1^2 - k h_2^2 \Delta\bar{\rho} (1 + \Delta\bar{\rho}) / \varepsilon}, \quad (12.49)$$

which exactly corresponds to the solution of an analogous problem obtained in (Strack 1976; Guo and Jiu 2007) with the use of flow description by a potential function.

Some particular cases:

(a) $\varepsilon \rightarrow 0$:

$$(h_2 - z)^2 = \frac{2Q_0}{k\Delta\bar{\rho}(1 + \Delta\bar{\rho})}x, \quad L = \frac{kh_2^2\Delta\bar{\rho}(1 + \Delta\bar{\rho})}{2Q_0}; \quad (12.50)$$

(b) $Q_0 \rightarrow 0$:

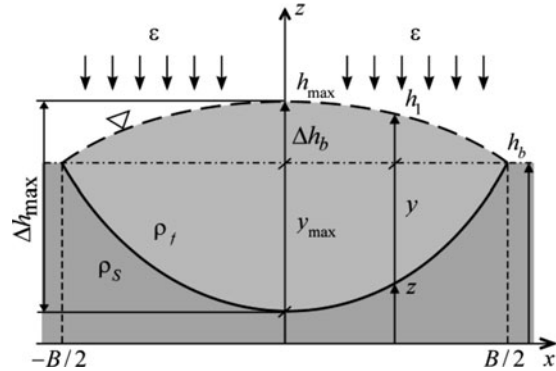
$$(h_2 - z)^2 = \frac{\varepsilon}{k\Delta\bar{\rho}(1 + \Delta\bar{\rho})}(2L - x)x, \quad L = h_2 \sqrt{\frac{k}{\varepsilon} \Delta\bar{\rho}(1 + \Delta\bar{\rho})}. \quad (12.51)$$

12.2.4 Freshwater Lens on an Elongated Oceanic Island

The two-dimensional steady-state problem formulation (Fig. 12.6) is reduced to solving the ordinary differential equation

$$\varepsilon x = -k(h_1 - z) \frac{dh_1}{dx}. \quad (12.52)$$

Fig. 12.6 Diagram of the model describing the formation of a rainwater lens on an elongated oceanic island



Integrating (12.8) from z to h_b (the left part) and from h_1 to h_b (the right part), we obtain:

$$h_1 = h_b(1 + \Delta\bar{\rho}) - \Delta\bar{\rho}z \quad (12.53)$$

(the head h_b is given in Fig. 12.6). Now, with the substitution $y = h_b - z$ ($dz = -dy$), Eq. 12.52 becomes

$$\epsilon dx^2 = -k\Delta\bar{\rho}(1 + \bar{\rho})dy^2. \quad (12.54)$$

The integration of this equation within intervals $0, B/2$ (the right part) and $y_{\max}, 0$ (the left part) allows us to find $y_{\max}$:

$$y_{\max}^2 = \frac{\epsilon B^2}{4k\Delta\bar{\rho}(1 + \Delta\bar{\rho})} \quad (12.55)$$

(B is island width).

The complete solution has the form

$$y^2 = \frac{\epsilon}{k\Delta\bar{\rho}(1 + \Delta\bar{\rho})} \left(\frac{B^2}{4} - x^2 \right). \quad (12.56)$$

The height of the freshwater dome above the reference plane:

$$h_{\max} = h_b + \Delta\bar{\rho}y_{\max}. \quad (12.56a)$$

The height of the freshwater dome above ocean surface:

$$\Delta h_b = h_{\max} - h_b = \Delta\bar{\rho}y_{\max}. \quad (12.56b)$$

The full thickness of fresh water in the center of the island:

$$\Delta h_{\max} = \Delta h + y_{\max} = \epsilon B^2 / 4k\Delta\bar{\rho}. \quad (12.56c)$$

The analytical solutions given in this section are convenient for preliminary (expert) estimates, which, at the main stages of hydrogeological studies in coastal areas, should be complemented by numerical solutions of appropriate problems (an example of such approach is given in Chap. 16).

12.3 Equilibrium for Saltwater Upconing Beneath a Partially Penetrating Well

The term “saltwater upconing” refers to the upward motion of deep saltwater into freshwater aquifers induced by pressure redistribution caused by pumping (Fig. 12.7). This process has been observed in coastal areas over the whole world where freshwater pumping increases degradation of coastal aquifer water quality, and in many mining fields with intensive drainage operations. Upconing of natural brines is often a cause of groundwater contamination; it might consequently result in a large social and environmental damage. An important example of the latter condition exists in the Korshunovsky ore deposit site (Eastern Siberia), where intensive drainage operations for the last 40 years have resulted in a large drawdown of the water table (Chap. 17).

The problem of upconing was formulated by Muskat and Wyckoff (1935), using the sharp-interface approach, in relation to saltwater coning beneath oil wells. Since then, there have been numerous investigations aimed at observing this phenomenon and simulating it with numerical and analytical models (see Reilly and Goodman 1985 for a review; Charnyi 1963; Bear 1972; Kisel and Abramov 1978; Essaid 1990; Motz 1992; Bower et al. 1999; Lin et al. 1999; Panday et al. 1993; Zhou et al. 2005).

Analytical solutions for saltwater (brine) upconing describe the motion of a sharp freshwater-saltwater interface (FSI). Although Diersch et al. (1984) and Zhou et al. (2005) showed that dispersion quantitatively and qualitatively influences the upconing process, the sharp-interface approach is considered to be an appropriate approximation for regional studies, when the transition zone between saltwater and freshwater is thin relative to the thickness of the aquifer (Bear 1979; Essaid 1990).

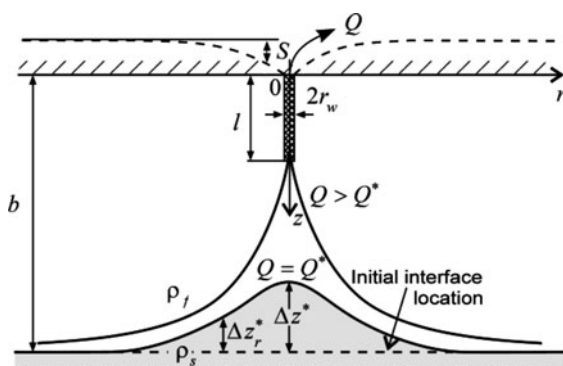


Fig. 12.7 A definition sketch for the saltwater upconing showing a partially penetrating well extracting water from a confined aquifer with a flat freshwater-saltwater initial interface

The operation of a partially penetrating well, whose screen taps the upper part of a water-bearing stratum (or, in a wider sense, a partially penetrating drainage contour) results in significant local drawdown that can cause underlying saltwater to migrate (to “*upcone*”) upward into the well (Fig. 12.7). In reality, the saltwater cone can either reach the well, leading to an increase in water-soluble salts in the pumped-out water (see Sect. 14.2.3), or become relatively stable at some distance from the screen. This depends on the well volumetric flow rate, the difference between fresh and saltwater density, and the characteristics of the well and the aquifer. The maximal possible well flow rate, Q^* , at which saltwater cone does not reach the well is referred to as *critical pumping rate*; this characteristic of the process corresponds to the value of Δz^* , i.e., the *critical rise of the freshwater–saltwater interface* along the axis $r = r_w$ (Fig. 12.7).

Notwithstanding the keen interest of many researchers in the upcone-formation problem and the large number of published studies, not well-developed theory for the relevant process is still available, because of its extreme complexity.

12.3.1 Problem Setting and Analysis of Existing Approaches and Solutions

Under the sharp-interface assumptions, two methods are applied to simulate saltwater upconing.

The first method is based on the assumption that the lower (heavier) liquid is stationary, so that the FSI behaves as an impervious boundary (or a streamline), and that the shape of this boundary beneath the partially penetrating pumping well does not affect the piezometric head distribution in the region occupied by the lighter liquid. Based on the Ghyben–Herzberg relation, the rise in the SFI (Fig. 12.7) is given by (Bear 1979; Motz 1992, 1995):

$$\Delta z_r = b - z(r) = \frac{1}{\Delta \rho} S(r, z = b), \quad (12.57)$$

where Δz_r is the rise of the freshwater-saltwater interface at the distance r from the well [L]; $S(r, z)$ is the drawdown at a point (r, z) [L]; b is the thickness of the freshwater zone [L].

The hydrostatic model (12.57) determines streamline coordinates for particles of freshwater moving along the FSI. The saltwater is assumed to adjust rapidly to the changes in fresh water stresses with a new equilibrium position of the FSI.

The hydrostatic model (12.57) realistically describes the relation between Δz_r and $S(r, z = b)$ as long as the rise of the FSI does not exceed some critical value, $\Delta z^* = \Delta z_r^* (r = r_w)$ (see Fig. 12.7 for notation). The latter corresponds to the height to which the cone will rise before instability occurs beneath the pumping well and relation between Δz^* and S (or Q) will not be *linear* any more. By other words, in case the upconed interface passed Δz^* , it reaches the pumping well with a sudden *jump*. Thus, salinization of the pumping well occurs only for $\Delta z > \Delta z^*$.

Characteristic Δz^* is normally expressed in $\theta(b-l)$, where θ is the ratio between (a) the critical interface rise and (b) the distance between the initial location of the interface ($z=b$) and the bottom of a well ($z=l$). Thus, Eq. 12.57 for the steady-state conditions results in the expression:

$$\Delta z^* = \theta(b-l) = \frac{1}{\Delta \bar{\rho}} S(r_w, z=b), \quad (12.58)$$

which can be used to determine the critical pumping rate. The value for θ , according to different investigations (Muskat 1937; Bear and Dagan 1964; Bennett et al. 1968; Schmorak and Mercado 1969; Bear 1979; Wirojanagud and Charbeneau 1985; Motz 1992, 1995; Bower et al. 1999), can vary from 0.25 to 0.89.

The critical rise corresponds to the critical pumping rate, Q^* , which is one of the integrated characteristics of the FST equilibrium. Estimation of this value is of a great practical importance since it is the highest possible production of fresh water without catching upconed saltwater into a well. A set of analytical solutions obtained for different conceptualization of hydrogeological settings can be used to determine $S(r_w, z=b) = f(Q)$, and then to obtain a relationship for the critical characteristics Q^* or/and Δz^* .

For example, from a solution for an aquifer overlaid by a leaky confining bed (Hantush 1964), Motz (1992) obtained an analytical solution for the critical pumping rate, where the relative critical rise, θ , of the FSI was assumed to be 0.3. The latter value was subject for debates (Motz 1995; Panday et al. 1993). Thus, the numerical simulation by Panday et al. (1993) performed for a particular area (the Geneva freshwater lens site) predicted a noticeably larger interface rise (up to 0.57) and a discharge rate than one would predict using the analytical solution presented by Motz (1992).

The uncertainty of the *a priori* assessment of the critical rise of the interface, Δz_r^* , in particular beneath the well, $\Delta z^* = \Delta z_r^*(r=r_w)$, can be avoided if two conditions are satisfied (Charnyi 1963; Bower et al. 1999). The first condition implies that the pressure in the freshwater region must be equal to the pressure across the stationary interface in saltwater region. The Ghyben–Herzberg relation is then transformed as follows:

$$\Delta z_r^* = \frac{1}{\Delta \bar{\rho}} S(r, z=b-\Delta z_r^*). \quad (12.59a)$$

The second condition requires that pressure gradients on both sides of the interface are equal in the critical state, which yields:

$$\frac{\partial S(r, z=b-\Delta z_r^*)}{\partial z} = -\Delta \bar{\rho}. \quad (12.59b)$$

Physically, the latter condition means that the potential velocity of the interface sinking under the effect of gravity $q_\rho = k_z \Delta \bar{\rho}$ is equal to the vertical Darcy velocity of water in point (r, z) , $q_z = -k_z \partial S / \partial z$, k_z is the vertical hydraulic conductivity. Strictly speaking, even when the interface is stationary, saltwater is still moving, forming a kind of circulation cell, as can be seen from numerical solutions of the problem (Zhou et al. 2005).

The system combining Eq. 12.59 was solved using iterative method (Bower et al. 1999), again for an aquifer overlaid by a leaky confining unit. In this calculation, Bower et al. (1999) obtained the critical interface rise ratio θ equal to 0.71. Although the values of the critical interface rise ratio and corresponding critical pumping rate should be relatively insensitive to changes in r_w , those authors kept the latter parameter in all graphical representations of the calculated values of Δz^* and Q^* .

The second method of analysis of the saltwater upconing is based on solving the Laplace equations for piezometric heads (Dagan and Bear 1972; Lin et al. 1999) or pressure (Kisel and Abramov 1978) in two regions occupied by freshwater and saltwater. Thus, via a linearized perturbation analysis, Dagan and Bear (1968) derived hydrodynamic equations for the rise of a saltwater cone $\Delta z(r, t)$ beneath a pumping well. In case of a short (compared to the freshwater zone) well and an infinite thickness of a saltwater aquifer, the position of the FSI directly underneath the pumping well ($r = 0$) can be derived from the equation (Dagan and Bear 1968; Schmorak and Mercado 1969):

$$\Delta z(0, t) = \frac{Q}{2\pi\Delta\bar{\rho}k_r(b-l)} \left[1 - \frac{1}{1+\tau} \right], \quad \tau = \frac{\Delta\bar{\rho}k_z}{2\phi(b-l)}t. \quad (12.60)$$

From (12.60), assuming $t \rightarrow \infty$, the critical rise of the interface $\Delta z^* = \theta(b-l)$ can be obtained. Therefore, the maximum possible pumping rate without pumping of saltwater is given by

$$Q^* = (\theta)2\pi k_r\Delta\bar{\rho}(b-l)^2. \quad (12.60a)$$

In this case, analytical solution (12.60) can be rewrite in the “elegant” dimensionless form as follows:

$$\Delta\bar{z} = \frac{Q}{Q^*} \frac{\tau}{1+\tau}, \quad \Delta\bar{z} = \frac{\Delta z(0, \tau)}{\Delta z^*}. \quad (12.60b)$$

Despite a certain progress was achieved during the last decades in understanding saltwater upconing, the existing analytical estimates of the critical pumping rate have certain limitations. Thus, one of the disadvantages of the described methods is that they cannot be used for predicting a change in the concentration of the upconed saltwater when the upconing interface passes Δz^* . In the literature, one can find only few references to the solutions for the case $Q > Q^*$ (Charnyi 1963; Kisel and Abramov 1978; Paster and Dagan 2008b). Unfortunately, they are obtained in rather complex and unclosed forms, which are not convenient for practical applications.

12.3.2 Analytical Solutions for the Critical Pumping Rate and the Critical Interface Rise

In this section, modified and approximate solutions are presented to estimate a critical pumping rate and the related critical interface rise that can be applied for an

anisotropic media and for an aquifer overlaid by impermeable or leaky confining beds. The assessment of the critical characteristics Q^* and $\Delta\bar{z}^*$ can be based on Eqs. 12.59a and 12.59b. This system of equations can be rewritten in a dimensionless form:

$$\Delta\bar{z}_r^* = \frac{\bar{S}}{\Delta\bar{\rho}}, \quad (12.61a)$$

$$\frac{\partial\bar{S}}{\partial\bar{z}} = -\Delta\bar{\rho}, \quad (12.61b)$$

where $\bar{S} = S(\bar{r}, \bar{z}^*)/b$, $\bar{r} = r/b$, $\bar{z} = z/b$, $\bar{z}^* = 1 - \Delta\bar{z}_r^*$, $\Delta\bar{z}_r^* = \Delta z_r^*/b$.

Equations 12.61a and 12.61b can be solved simultaneously for a given type of groundwater reservoir conditions. Further down, it is shown how the model (12.61a–12.61b) works when applied to study the upconing process in two types of confined aquifers. To determine the critical value of Δz^* and the respective value of Q^* , it is sufficient to limit the analysis to the case of $r = r_w$.

12.3.2.1 Confined Aquifer with Impermeable Top and Bottom

The steady-state drawdown $\bar{S} = \bar{S}(\bar{r}, \bar{z})$ and its derivative $\partial\bar{S}/\partial\bar{z}$ for an aquifer with a constant-head radial boundary at $r = R$ is given by Hantush (1964) and Verigin et al. (1977):

$$\bar{S} = \frac{Q}{4\pi T b} \left(2 \ln \frac{\bar{R}}{\bar{r}} + f_s \right), \quad \frac{\partial\bar{S}}{\partial\bar{z}} = \frac{Q}{4\pi T b} f'_s; \quad (12.62a)$$

$$f_s \equiv f_s(\bar{r}, \bar{z}) = \frac{4}{\pi\beta} \sum_{n=1}^{\infty} \frac{1}{n} \sin(n\pi\beta) \cos(n\pi\bar{z}) K_0(n\pi\bar{r}); \quad (12.62b)$$

$$f'_s \equiv f'_s(\bar{r}, \bar{z}) = -\frac{4}{\beta} \sum_{n=1}^{\infty} \sin(n\pi\beta) \sin(n\pi\bar{z}) K_0(n\pi\bar{r}); \quad (12.62c)$$

$\bar{z} = z/b$; $\bar{r} = r/\kappa b$; $\bar{R} = R/\kappa b$; $\beta = l/b$; $T = k_r b$; $\bar{S} = S/b$ is the relative drawdown; $\kappa = \sqrt{k_r/k_z}$ is the anisotropy coefficient; k_r and k_z are hydraulic conductivities of the aquifer in lateral and vertical directions [LT^{-1}]; l is the screen length [L]; R is the radius of influence of pumping [L]; hereafter, $\bar{z} = \bar{z}(\bar{r})$, so that the dimensionless value of saltwater cone rise beneath the well is (Fig. 12.7), $\Delta\bar{z}^* = 1 - \bar{z}(r_w)$. Note, that the series (12.62b) and (12.62c) slowly converge for small $\bar{r}$ ($\bar{r} < 1$).

Substituting Eq. 12.62 for $\bar{S}$ and $\partial\bar{S}/\partial\bar{z}$ in Eq. 12.61, and expressing those for the critical conditions (when $\bar{r} = \bar{r}_w$ and $\bar{z} \equiv \bar{z}^* = 1 - \Delta\bar{z}^*$), Eq. 12.61 can be transformed in:

$$\begin{aligned} \bar{Q}^* &= \frac{Q^*}{T b \Delta\bar{\rho}} = \frac{2\pi(1 - \bar{z})}{\ln \bar{R}/\bar{r}_w + f_s(\bar{r}_w, \bar{z})/2}, \\ \bar{Q}^* &= \frac{Q^*}{T b \Delta\bar{\rho}} = -\frac{2\pi}{f'_s(\bar{r}_w, \bar{z})/2}. \end{aligned} \quad (12.63)$$

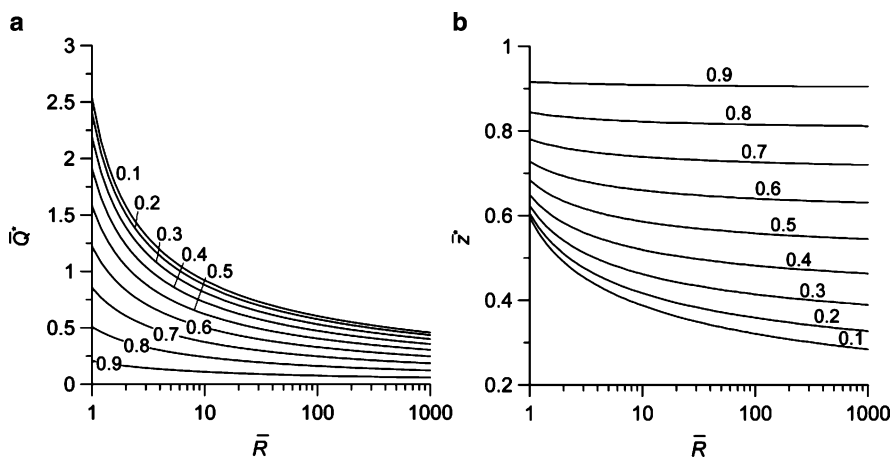


Fig. 12.8 Calculated values of $\bar{Q}^*$ (a), $\bar{z}^*$ (b) as functions of $\bar{R}$; the numbers against curves correspond to different β ; $\bar{r}_w = 0.001$

Eq. 12.63 were solved numerically assuming $\bar{r}_w = 0.001$ as shown in Fig. 12.8. One important conclusion (Fig. 12.8) was that the relative critical rise of the freshwater–saltwater interface $\theta = \Delta\bar{z}^*/(1 - \beta)$ ranges between 0.75 ($\beta = 0.1$) and 0.9 ($\beta = 0.7$) for $\bar{R} = 100$, exceeding $\theta = 0.3$ often used in estimates of critical conditions (Motz 1995; Panday et al. 1993).

The critical pumping rate, $\bar{Q}^*$, derived from Eqs. 12.63 had a negligible sensitivity to the dimensionless radius of the well, $\bar{r}_w$, within the practically significant domain $\bar{r}_w < 0.01$ (Fig. 12.9). This can take place if function f_s , Eq. 12.62b, has an alternative structure which includes a logarithmic term $\sim \ln(\bar{r})$. Indeed, approximation of function f_s , Eq. 12.62b, by a simplified analytical formula

$$f_s = 2 \ln(\bar{r}/\beta) + 2 \ln \beta + A(\bar{z}), \quad (12.64)$$

$$A(\bar{z}) = 0.1 + \frac{0.8}{\bar{z}} + \frac{0.18}{\bar{z}^2} + 4\beta \exp\left(\frac{1}{\bar{z}} - 1\right) \ln(1 + \beta), \quad (12.64a)$$

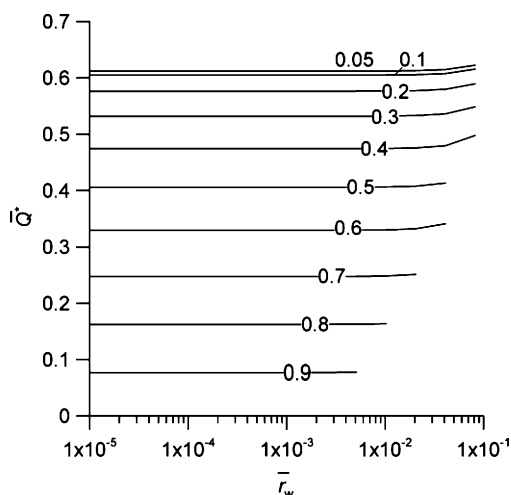
allows us to transform Eqs. 12.63 as follows:

$$\begin{aligned} \bar{Q}^* &= \frac{2\pi(1 - \bar{z})}{\ln(\bar{R}) + A(\bar{z})/2}, \\ \bar{Q}^* &= \frac{2\pi}{A'(\bar{z})/2}; \end{aligned} \quad (12.65)$$

here

$$A'(\bar{z}) = f'_s = - \left[\frac{0.8}{\bar{z}^2} + \frac{0.36}{\bar{z}^3} + \frac{4\beta}{\bar{z}^2} \cdot \ln(1 + \beta) \exp\left(\frac{1}{\bar{z}} - 1\right) \right]. \quad (12.65a)$$

Fig. 12.9 Relative critical pumping rate, $\bar{Q}^*$, as a function of $\bar{r}_w$ for different β (cipher of curves); $\bar{R} = 100$



Equation 12.64 satisfactory approximates Eq. 12.62b for $\beta < 0.4$ – 0.5 and $\bar{r}_w/\beta < 1$. The form of Eqs. 12.65 leads to the conclusion that for the conditions $r_w/\kappa l < 1$ (that commonly occurs), the critical pumping rate (Q^*) and the critical rise of the FSI (Δz^*) are independent of the radius of well.

12.3.2.2 Confined Leaky Aquifer

Steady-state drawdown $\bar{S} = \bar{S}(\bar{r}, \bar{z})$ in an aquifer recharged by leakage from an upper aquifer with constant hydraulic head through a semi-permeable layer is given by Hantush (1964):

$$\bar{S} = \frac{Q}{4\pi T b} (2K_0(r/B) + f_s); \quad (12.66)$$

here $1/B = (k_0/b_0 T)^{1/2}$ is a combined parameter characterizing hydrodynamic interaction between the aquifers; k_0 and b_0 are hydraulic conductivity and thickness of the aquitard (k_0/b_0 is a leakage of the confining unit [T^{-1}]).

Taking a partial derivative of $\bar{S}$ with respect to $\bar{z}$ transforms Eq. 12.66 into Eq. 12.62b. If the condition $r_w/B \ll 1$ is satisfied, $K_0(r_w/B)$ can be substituted by $\ln(B/r_w)$. In this case, the dimensionless critical pumping rate can be obtained from the Eq. 12.65 with B substituting for R ; consequently, all the transformations presented above can be applied for omitting r_w .

In addition to the relationships considered above, of some interest are models giving an insight into variations in salt concentration in the pump-out well (when $Q > Q^*$). Thus, the information stemmed from mathematical description of the process under condition $Q > Q^*$ is of practical importance in predicting the quality of drainage water during dewatering of mineral deposits. Additionally, the better understanding of saltwater upconing will help in interpretation of hydrochemical data

obtained from pumping tests in coastal areas. Therefore, additional efforts regarding to further development of the models describing solutes transport under such conditions are needed (Sect. 14.2.3).

For example, the use of mathematical modeling (Zhou et al. 2005) showed that the dispersion of the interface shifts the estimates of the limiting well flow rate toward its decrease, and circulation of brine within the cone increases the height of its rise. It was noted that the reverse process (cone flattening after the pumping) is ceased is lengthy (the return of the interface to the initial position is extremely slow). It takes a long time for the upconed saltwater to migrate back to the original horizontal transition zone prior to pumping. This feature of the process should be taken into account when rehabilitation measures at water intake are designed: restarting of a water intake well after its salinization can be justified only after a very long time.

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Chapter 13

Dynamics of Saltwater–Freshwater Interface

The displacement of a fluid by another one of different density and viscosity represents a problem of fundamental interest. It finds applications in situations ranging from enhanced oil recovery and the spreading of pollutants in groundwater reservoirs, to processes accompanying CO₂ sequestration in the deep geological formations. In the first part of this chapter (Sect. 13.1) the linear (unidirectional in the horizontal plane) and radial movement of the interface between displacing and displaced fluids in a confined homogeneous aquifer is analyzed. In the second part of the chapter (Sect. 13.2) we will examine how some ideas of the two-phase flow theory can be used to model the migration of brine in fresh water aquifer systems.

13.1 Two-Dimensional Profile Models for Immiscible Fluids Interface Displacement

Let us assume that fluids differ in physical properties, density, $\rho_{1,2}$, and viscosity, $\mu_{1,2}$ (the subscript 1 refers to the displacing solution and the subscript 2, to the displaced one). A theoretical analysis shows that such displacement is accompanied by a “deformation” of the saltwater–freshwater interface due to gravity (Fig. 13.1). Indeed, as can be seen from the schematic representation of the process in Fig. 13.1a, even in the initial moments, when the interface is vertical and close to the inflow boundary, pressure gradients in the denser fluid near the bed floor are greater than its gradients near the bed roof by the value $\sim mg(\rho_2 - \rho_1)$. The pressure differential makes the particles of the denser water in the bottom part of the bed to move with higher velocities, such that the interface becomes inclined. Additional influence on the character and shape of the moving interface is due to the different viscosities of the moving solutions.

Studying this class of problems is the focus of many fundamental works (Charnyi 1963; Bear 1972; Hellström et al. 1988 and others). They serve as the basis for the models considered in this study, describing linear and radial flows of fluids with different density and viscosity.

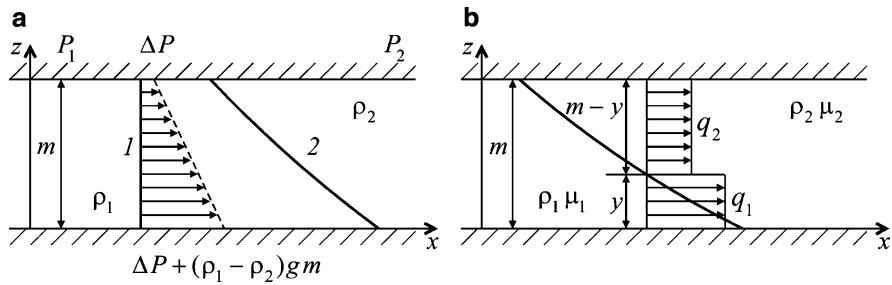


Fig. 13.1 Deformation of an interface between two fluids due to contrast in density. **(a)** The vertical distribution of initial pressures ($t = 0$) for the case $\rho_2 > \rho_1$ (Muskat 1937) (1 and 2 are interface positions at $t = 0$ and $t > 0$); **(b)** flow fragmentation for the derivation of interface motion equation, rectilinear problem (arrows show the distribution of specific discharge q_1 and q_2) (Bear 1972)

13.1.1 Linear Displacement

13.1.1.1 Governing Equations

Consider the continuity equation, which should be valid in domains 1 and 2 , occupied by the displacing and displaced fluids, respectively (Fig. 13.1b):

$$\frac{\partial q_x}{\partial x} + \frac{\partial q_z}{\partial z} = 0, \quad (13.1)$$

where q_x and q_z are the lateral and vertical components of specific discharge, and q_x varies only with x .

The integration of this equation over z from 0 to y for domain 1 yields:

$$\int_0^y \frac{\partial q_x}{\partial x} dz + \int_0^y \frac{\partial q_z}{\partial z} dz = 0; \quad (13.2)$$

here $y = y(x, t)$ is the current coordinate of the interface (Fig. 13.1b). Using *Leibnitz* rule (Bear 1972, p 534), we obtain

$$\frac{\partial}{\partial x} \int_0^y q_x dz - q_x \Big|_{z=y} \frac{\partial y}{\partial x} + q_z \Big|_{z=y} - q_z \Big|_{z=0} = 0. \quad (13.3)$$

Since $q_z \Big|_{z=0} = 0$, $q_z \Big|_{z=y} / \phi = dy/dt$, $q_x \Big|_{z=y} / \phi = (dx/dt) \Big|_{z=y}$ and $dy/dt = \partial y / \partial t + (\partial y / \partial x)(dx/dt) \Big|_{z=y}$ (ϕ is the aquifer porosity), we have:

$$\frac{\partial Q_{x1}}{\partial x} + \phi \frac{\partial y}{\partial t} = 0, \quad (13.4)$$

where $Q_{x1} = \int_0^y q_x dz$ is the flow rate of the displacing fluid in the section $[0, y]$.

Applying the same transformations to the continuity Eq. 13.1, considered for the displaced-fluid domain 2, we obtain a similar equation for the flow rate Q_{x2} in differential form

$$\frac{\partial Q_{x2}}{\partial x} + \phi \frac{\partial(m-y)}{\partial t} = 0, \quad (13.5)$$

where $Q_{x2} = \int_y^m q_x dz$ is the flow rate of the displaced fluid in the section $[y, m]$.

Adding (13.4) and (13.5), we obtain

$$\frac{\partial(Q_{x1} + Q_{x2})}{\partial x} = 0. \quad (13.6)$$

This means that the total flow rate, $Q = Q_{x1} + Q_{x2}$, does not depend on the coordinate x and is generally determined by the current time $Q = Q(t)$.

To simplify the analysis below, we can use the Dupuit–Forchheimer assumption that the Darcy velocity does not vary over the depth in any model section x . Now (Bear 1972):

$$Q_{x1} = q_1 y = -\frac{K\rho_1 g}{\mu_1} \frac{\partial h_1}{\partial x} y, \quad (13.7)$$

$$Q_{x2} = q_2(m-y) = -\frac{K\rho_2 g}{\mu_2} \frac{\partial h_2}{\partial x} (m-y), \quad (13.7a)$$

where $h_{1,2} = h_{1,2}(x, t) = P_{1,2}/\rho_{1,2}g + z$, K is the absolute permeability. The condition that the pressure values in the fluids on the interface are equal, $P_1 = P_2$, implies that

$$\rho_1 h_1 - \rho_2 h_2 = (\rho_1 - \rho_2)z \text{ in the point } z = y, \quad (13.8)$$

or

$$\rho_1 \frac{\partial h_1}{\partial x} - \rho_2 \frac{\partial h_2}{\partial x} = (\rho_1 - \rho_2) \frac{\partial y}{\partial x}. \quad (13.8a)$$

Combining the above equations, we obtain:

$$\frac{\partial}{\partial x} \left[y \frac{Q - k \Delta \bar{\rho} (m-y) \partial y / \partial x}{y + \bar{\mu} (m-y)} \right] + \phi \frac{\partial y}{\partial t} = 0, \quad (13.9)$$

where $\Delta \bar{\rho} = (\rho_1 - \rho_2)/\rho_2$ is density gradient, $\bar{\mu} = \mu_1/\mu_2$ is relative viscosity, $k = K\rho_2 g/\mu_2$ is hydraulic conductivity for freshwater.

A similar procedure can be used to construct a model describing the motion of the interface in a vertically heterogeneous bed with permeability varying across the bedding, i.e., $K = K(z)$. To do this, we write the expressions for flow characteristics Q_{x1} (13.7) and Q_{x2} (13.8) as

$$Q_{x1} = q_1 y = -\frac{\rho_1 g}{\mu_1} T(0, y) \frac{\partial h_1}{\partial x}, \quad (13.10)$$

$$Q_{x2} = q_2(m - y) = -\frac{\rho_2 g}{\mu_2} T(y, m) \frac{\partial h_2}{\partial x}, \quad (13.10a)$$

where $T(0, y) = \int_0^y K(z) dz$; $T(y, m) = \int_y^m K(z) dz$. By transformations similar to those considered above, we obtain

$$\frac{\partial}{\partial x} \left[T(0, y) \frac{Q - \frac{1}{\mu_2} (\rho_1 - \rho_2) g T(y, m) \partial y / \partial x}{T(0, y) + \bar{\mu} T(y, m)} \right] + \phi \frac{\partial y}{\partial t} = 0. \quad (13.11)$$

Thus, solution of a problem on displacement of a fluid with density ρ_1 and viscosity μ_1 by a fluid with density ρ_2 and viscosity μ_2 comes to the integration of nonlinear differential equations of parabolic type, Eqs. 13.9 and 13.11. Numerical methods are commonly used for this purpose. Approximate solutions for some particular cases can be obtained by analytical transformations.

When the difference between fluid viscosities can be neglected ($\mu_1 = \mu_2$, $\bar{\mu} = 1$), which is true for the case of migration of inorganic salt solutions, Eq. 13.9 can be simplified

$$\frac{\partial}{\partial x} \left[y \frac{Q - k \Delta \bar{\rho} (m - y) \partial y / \partial x}{m} \right] + \phi \frac{\partial y}{\partial t} = 0, \quad (13.12)$$

and transformed into the quasi-one-dimensional form

$$\frac{\partial \bar{y}}{\partial \bar{x}} - G \frac{\partial}{\partial \bar{x}} \left(\bar{y} (1 - \bar{y}) \frac{\partial \bar{y}}{\partial \bar{x}} \right) + \frac{\partial \bar{y}}{\partial \bar{t}} = 0, \quad (13.13)$$

where $\bar{y} = y/m$, $\bar{x} = x/m$, $\bar{t} = Qt/m^2\phi$, $G = k \Delta \bar{\rho} m / Q$ (see Eq. 12.19).

The coefficient G in Eq. 13.13 has the physical meaning of the ratio between parameters governing the rate of natural (density-induced) and forced (under the effect of hydraulic gradient) advection. As can be readily seen, $G \approx \Delta \bar{\rho} / I_{av}$, where I_{av} is the mean hydrodynamic gradient.

Equation 13.13 is a partial differential equation of parabolic type. By its form, it resembles an advective transport equation with nonlinear (depending on the value of function, in this case, $\bar{y}$) dispersion, where function $\bar{y}$ is an analogue of the relative concentration $\bar{C}$, and the boundary condition ($\bar{y}(\bar{x} = 0) = 1$) formally coincides with the condition for the fundamental concentration problem ($\bar{C}(x = 0) = 1$). Note that in this case, the dispersion term of Eq. 13.13 has an extremum at $\bar{y} = 1/2$ and vanishes on the boundaries of the interval $\bar{y} = 0$ and $\bar{y} = 1$.

13.1.1.2 A Numerical Solution of Eq. 13.13

Equation 13.13 was derived under certain simplifying assumptions and the relevant transport model can be considered as a highly simplified model, an initial mathematical approximation of displacement of two fluids in a 2D porous *isotropic* medium.

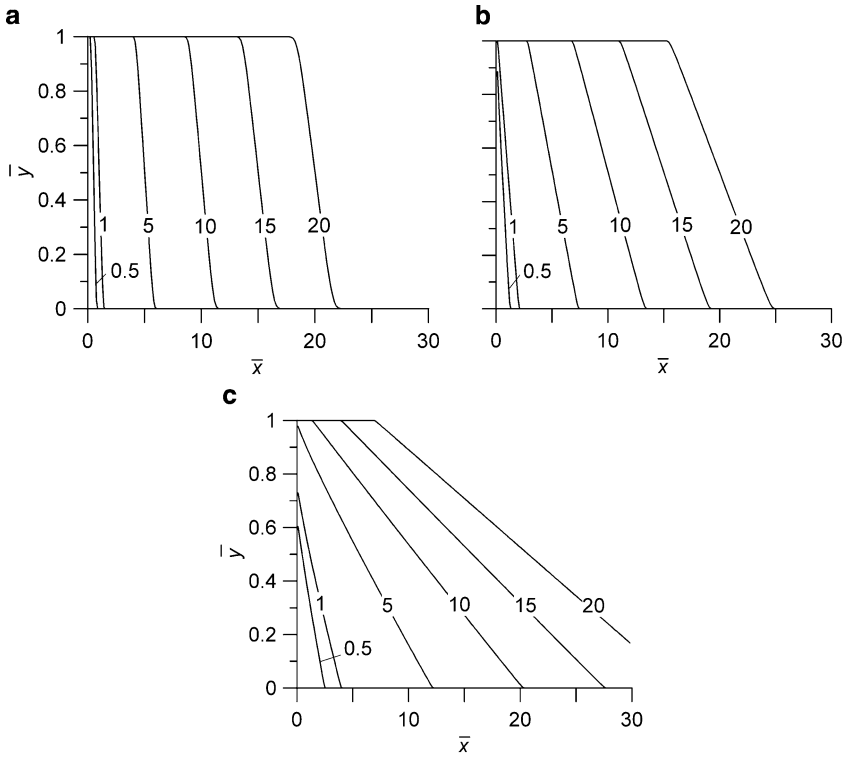


Fig. 13.2 The formation of the tilted interface between two fluids with different densities. (a, b, c) model results, G : (a) 0.1, (b) 1, (c) 10 (numbers at curves are values of dimensionless time $\bar{t}$)

The “benchmark” solutions of Eq. 13.13, obtained by numerical integration for particular cases of $G = 0.1, 1$, and 10, are plotted in Fig. 13.2. It can be seen that the sought-for function $\bar{y} = f(\bar{x})$ has a nearly linear form with $\bar{y}|_{\bar{x}=\bar{t}} \approx 0.5$, i.e., the median point of the tilted interface moves with a constant velocity equal to the actual fluid velocity. Moreover, analysis of the plots (Fig. 13.2) shows that the length of interface projection onto the horizontal plane is $\Delta\bar{x}_p = (\bar{x}_{\bar{y}=0} - \bar{x}_{\bar{y}=1}) \approx 2\sqrt{G\bar{t}}$.

13.1.1.3 Approximate Analytical Solutions for the Movement of the Interface in an Isotropic Aquifer

One of the solutions for 1D unlimited domain, $-\infty < \bar{x} < \infty$, can be obtained if we assume that the initially vertical interface,

$$\bar{y}(\bar{x}, 0) = \begin{cases} 1, & \bar{x} \leq \bar{x}_0 \\ 0, & \bar{x} > \bar{x}_0, \end{cases}$$

rotates toward an equilibrium position $\bar{x} = \bar{t}$ as in a case of absence of inflow discharge (Gemtzi and Tolikas 2004)

$$\bar{y}(\bar{x}, \bar{t}) = \begin{cases} 1, & \bar{x} \leq \bar{x}_1(\bar{t}) \\ \frac{\bar{x}_2(\bar{t}) - \bar{x}}{\bar{x}_2(\bar{t}) - \bar{x}_1(\bar{t})}, & \bar{x}_1(\bar{t}) < \bar{x} < \bar{x}_2(\bar{t}) \\ 0, & \bar{x} \geq \bar{x}_2(\bar{t}), \end{cases} \quad (13.14)$$

$$\bar{x}_1(\bar{t}) = \bar{x}_0 + \bar{t} - \sqrt{G\bar{t}}, \quad \bar{x}_2(\bar{t}) = \bar{x}_0 + \bar{t} + \sqrt{G\bar{t}}, \quad (13.14a)$$

whence $\Delta\bar{x}_p = \bar{x}_2 - \bar{x}_1 = 2\sqrt{G\bar{t}}$, which is in agreement with numerical solutions of the problem. Here $\bar{x}_1$ and $\bar{x}_2$ are locations of interface tip and toe. The relationship between $\bar{x}_1$ and $\bar{x}_2$, Eq. 13.14a, shows that the upper half of the interface moves at the same velocity as the bottom half of the interface, but in the opposite direction.

Another approximate solution of the problem can be obtained by a transformation of Eq. 13.13 with the introduction of an auxiliary integral function (Charnyi 1963)

$$u(\bar{y}) = \int_0^{\bar{y}} \bar{y}(1 - \bar{y}) d\bar{y} = \frac{1}{2} \bar{y}^2 \left(1 - \frac{2}{3} \bar{y} \right). \quad (13.15)$$

Since in this case

$$\frac{\partial \bar{y}}{\partial \bar{x}} = \frac{\partial u}{\partial \bar{x}} \bigg/ \frac{du}{d\bar{y}} = \frac{1}{\bar{y}(1 - \bar{y})} \frac{\partial u}{\partial \bar{x}} \quad \text{and} \quad \frac{\partial \bar{y}}{\partial \bar{t}} = \frac{\partial u}{\partial \bar{t}} \bigg/ \frac{du}{d\bar{y}} = \frac{1}{\bar{y}(1 - \bar{y})} \frac{\partial u}{\partial \bar{t}}, \quad (13.15a)$$

the Eq. 13.13 takes the form

$$\frac{\partial u}{\partial \bar{t}} + \frac{\partial u}{\partial \bar{x}} - D(\bar{y}) \frac{\partial^2 u}{\partial \bar{x}^2} = 0, \quad (13.16)$$

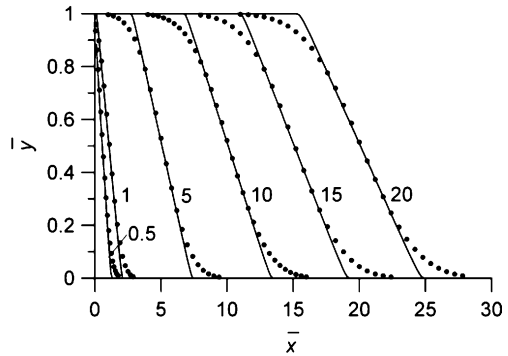
similar to the advection–dispersion equation with the dispersion coefficient depending on the sought-for function

$$D(\bar{y}) = G\bar{y}(1 - \bar{y}). \quad (13.16a)$$

The parabolic dependence (13.16a) becomes zero when $\bar{y} = 0$ and $\bar{y} = 1$ and has a maximum equal to $G/4$ at $\bar{y} = 1/2$. For further approximate estimates, we take the mean $D(\bar{y}) = D = G/8$. Now the solution of Eq. 13.16 with the constant boundary conditions

$$u(\bar{t} = 0) = 0 \quad [\bar{y}(\bar{t} = 0) = 0] \quad \text{and} \quad u(\bar{x} = 0) = u_0 = \frac{1}{6} \quad [\bar{y}(\bar{x} = 0) = 1],$$

Fig. 13.3 Comparison of the analytical, Eq. 13.17 (dots), and simulation (solid lines) results for interface dimensionless elevation. $G = 1$. Numbers at curves are the values of dimensionless time, $\bar{t}$



can be represented, by analogy with the solution of the fundamental problem of advection dispersion, in the form:

$$3\bar{y}^2 \left(1 - \frac{2}{3}\bar{y} \right) = \frac{1}{2} [\text{erfc}(\xi_1) + e^\eta \text{erfc}(\xi_1)], \quad (13.17)$$

$$\xi_1 = \frac{\bar{x} - \bar{t}}{2\sqrt{G\bar{t}/8}}, \quad \xi_1 = \frac{\bar{x} + \bar{t}}{2\sqrt{G\bar{t}/8}}, \quad \eta = \frac{8\bar{x}}{G}. \quad (13.17a)$$

The plots of the function $\bar{y}(\bar{x}, \bar{t})$, given in Fig. 13.3, demonstrate the acceptable accuracy of the calculated position of interface between liquids in the domain $0.1 < \bar{y} < 0.9$.

13.1.1.4 Some Asymptotic Assessments for an Anisotropic Aquifer

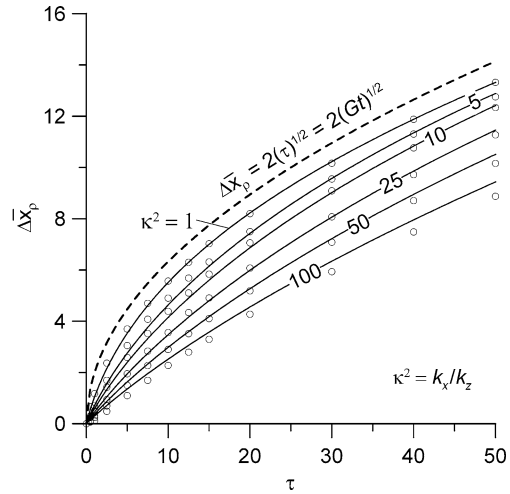
In addition to the above analysis, we give two more approximate solutions to the problem of formation of a tilted interface between two fluids in an anisotropic aquifer with an infinite length. Thus, from theoretical analysis (Gardner et al. 1962; Hellström et al. 1988) it can be shown that in the initial moments, when $t \ll \kappa^2 \phi m / k_x \Delta \bar{\rho}$, the anisotropic system exhibits the following asymptotic behavior:

$$\Delta \bar{x}_\rho \approx \xi_1 \frac{k_x \Delta \bar{\rho}}{m \phi \kappa} t, \quad (13.18)$$

where $\Delta \bar{x}_\rho = \Delta x_\rho / m$ is the dimensionless length of the projection of interface onto the horizontal plane (as in the previous process conceptualization, Sect. 13.1.1.2); $\kappa = \sqrt{k_x / k_z}$ is the anisotropy factor (> 1); a constant ξ_1 varies from $0.915 \cdot 16 / \pi^2 \approx 1.48$ (Hellström et al. 1988) to $\sqrt{3} \approx 1.73$ (Gardner et al. 1962). Thus, function $\Delta \bar{x}_\rho$ linearly depends on time, t , and inversely depends on the anisotropy, κ .

Behavior of $\Delta \bar{x}_\rho$ (13.18) at the initial stage of the displacement (when the dimensionless time, $\tau = k_x \Delta \bar{\rho} t / m \phi < 1 - 5$) in anisotropic aquifer is in good

Fig. 13.4 Comparison of results of 2D numerical analysis (using SEAWAT code with the model domain discretization by the grid 3000×90) of the process in an anisotropy confined aquifer (empty circles) with analytical approximation, Eq. 13.19 (solid curves); dashed curve corresponds to approximate analytical solution (13.14) for an isotropic aquifer



agreement with numerical simulation, $\Delta\bar{x}_p \sim t$ (Fig. 13.4). Later, however, the functional relationship between $\Delta\bar{x}_p$ and t becomes more complex. To calculate $\Delta\bar{x}_p$, x -coordinates of the intersection of 50%-isoconcentration line with the top and bottom of the aquifer were used. Strictly speaking artificial dispersion can affect the slope of the interface, but in the run simulations this effect is of a second order due to fine-grid model domain refinement.

The model results indicate that the displacement process is sensitive with respect to changes in anisotropy factor, κ , when $\kappa > 1$ ($k_z < k_x$). This belongs to the range of commonly observed hydrogeological data: in most of the studied groundwater formations the horizontal hydraulic conductivity is significantly greater than the vertical hydraulic conductivity. Contrarily, model scenarios for less common situations, when $\kappa < 1$, do not differ much from the isotropic case, $\kappa = 1$. In whole, the results of this study indicate that an increase in aquifer vertical anisotropy causes a decrease in the process characteristics $\Delta\bar{x}_p$ (Fig. 13.4).

The observed model curves, $\Delta\bar{x}_p = f(\tau)$ (Fig. 13.4), can be approximated by analytical formula as follows

$$\Delta\bar{x}_p \approx \xi_2 \left[1 - \exp \left(-\xi_3(\kappa) \frac{\sqrt{\tau}}{\kappa} \right) \right] \sqrt{\tau} \quad (\kappa \geq 1), \quad (13.19)$$

where $\xi_2 = 1.89$; $\xi_3(\kappa) = 0.81 \sqrt[3]{\kappa}$; $\tau = k_x \Delta \bar{\rho} t / m \phi$. Formula (13.19) can be used for practical purposes when the coefficient κ^2 does not exceed 100.

Model data and the proposed relationship demonstrate the following dynamics of the pressure-driven interface between two fluids of different densities and identical viscosities:

- (1) the initially vertical interface gradually tilts longitudinally because of the density difference; the interface has an almost linear shape;

- (2) the median point of the tilted interface moves with a constant (mid-depth) velocity equal to the actual fluid velocity;
- (3) at initial moments, the length of the projection of the interface onto the base of the model depends on the anisotropy factor, κ , and increases with a constant rate, $d\Delta\bar{x}_p(\tau)/d\tau = \text{const}$;
- (4) at a late time, function $\Delta\bar{x}_p \sim \sqrt{\tau}$, thus, the gradient $d\Delta\bar{x}_p(\tau)/d\tau$ being weakly sensitive to aquifer anisotropy slows down over time.

Finally, a comparison of approximate solution (13.14) against the performed simulation (scenario $\kappa = 1$, Fig. 13.4) shows that the simplified analytical model overestimates the $\Delta\bar{x}_p$ characteristics of the displacement process under consideration. The observed disagreement of the two compared results can be explained by the fact that the referred analytical model neglects the vertical resistance to flow. This effect is critical for all types of models assuming the Dupuit-Forchheimer approximation because in the vicinity of the interface subhorizontal velocity field undergoes wave-like fluctuations.

13.1.2 Radial Displacement

Disposal of brine in freshwater aquifer using well injection results in forming a brine plume with sloping interface between the displaced and displacing immiscible fluids. If dispersion effects are not taken into account, the contact between fluids is sharp, and the dynamics of its motion and its shape are only dependent on discharge rate and the density contrast between the brine body and the surrounding formation water.

The problem is commonly considered in a conventionally confined formulation, when the displacement of formation water takes place throughout the bed thickness, so that the brine–freshwater interface has contact points with both bed top and bottom. However, when salt water is poured into a well at low rate, the apex of the cone-like saltwater body may remain in a suspended position, not reaching the bed roof, over a long time.

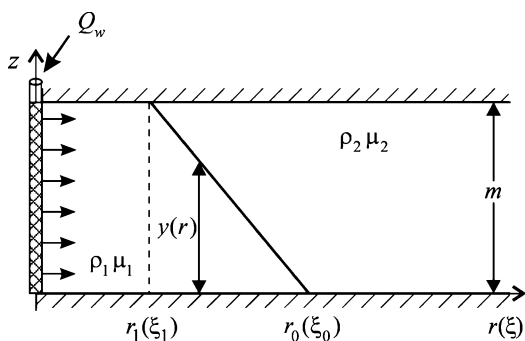
13.1.2.1 Confined Displacement

An analogue of Eq. 13.9 for the radial flow (Fig. 13.5) is the equation (Charnyi 1963)

$$\frac{\partial}{\partial r} \left[ry \frac{Q_w/2\pi r - k\Delta\bar{p}(m-y)\partial y/\partial r}{y + \bar{\mu}(m-y)} \right] + \phi r \frac{\partial y}{\partial t} = 0, \quad (13.20)$$

derived under the same Dupuit–Forchheimer assumption; here r is the radial coordinate, Q_w is the volumetric well recharge rate [L^3T^{-1}], $\bar{\mu} = \mu_1/\mu_2$, $\Delta\bar{p} = (\rho_1 - \rho_2)/\rho_2$, $k = K\rho_2g/\mu_2$ is the hydraulic conductivity in the freshwater domain [LT^{-1}].

Fig. 13.5 Schematic diagram for the derivation of equation describing the axially moving interface between the displacing and displaced fluids



To find a self-similar solution, we introduce the dimensionless variables:

$$\bar{y} = \frac{y}{m}, \quad \xi = \frac{r}{\sqrt{Q_w t / \pi m \phi}} \equiv \frac{r}{r^*}, \quad (13.21)$$

(r^* is the coordinate of the piston-like displacement front at $\Delta\rho = 0$), allowing Eq. 13.20 to be transformed into

$$\xi^2 \frac{d\bar{y}}{d\xi} - \frac{d}{d\xi} \left[\frac{\bar{y}}{\bar{y} + \bar{\mu}(1 - \bar{y})} - G \frac{\bar{y}(1 - \bar{y})}{\bar{y} + \bar{\mu}(1 - \bar{y})} \xi \frac{d\bar{y}}{d\xi} \right] = 0, \quad (13.22)$$

where $G = 2\pi k m^2 \Delta\bar{\rho} / Q_w$ is a dimensionless parameter characterizing the role of the gravity factor in case of axially symmetric flow. If we assume that the radial displacement is governed by effective specific yield, $Q = Q_w / 2\pi m$, we come to Eq. 12.19. Equation 13.22 is an ordinary linear differential equation, the fact that makes its solution much easier than in the case of the rectilinear flow with a constant rate Eq. 13.13.

First, as before, we consider the case where viscosity variations can be neglected, $\bar{\mu} = 1$. Now Eq. 13.22 becomes

$$\xi^2 \frac{d\bar{y}}{d\xi} - \frac{d}{d\xi} \left[\bar{y} - G\bar{y}(1 - \bar{y}) \xi \frac{d\bar{y}}{d\xi} \right] = 0, \quad (13.23)$$

or

$$\frac{1}{G} (1 - \xi^2) \frac{d\bar{y}}{d\xi} - (1 - 2\bar{y}) \xi \left(\frac{d\bar{y}}{d\xi} \right)^2 - \bar{y}(1 - \bar{y}) \frac{d\bar{y}}{d\xi} + \bar{y}(1 - \bar{y}) \xi \frac{d^2\bar{y}}{d\xi^2} = 0. \quad (13.24)$$

Suppose that ξ_0 and ξ_1 are dimensionless abscissas of the intersection points of the interface between waters with different densities and the aquifer bottom and top ($\xi_0 > \xi_1$ at $\rho_2 > \rho_1$), i.e., the coordinate ξ_0 corresponds to the value $\bar{y} = 0$ of the dimensionless function, while the coordinate ξ_1 corresponds to $\bar{y} = 1$ (Fig. 13.5). Now, Eq. 13.24 yields

$$\frac{d\bar{y}}{d\xi} \Big|_{\bar{y}=0} = \frac{1}{G} \left(\frac{1}{\xi_0} - \xi_0 \right), \quad \frac{d\bar{y}}{d\xi} \Big|_{\bar{y}=1} = -\frac{1}{G} \left(\frac{1}{\xi_1} - \xi_1 \right). \quad (13.25)$$

Next, suppose that function $\bar{y}(\xi)$ is linear in the range $\xi_1 \leq \xi \leq \xi_0$:

$$\bar{y}(\xi) = a(\xi - \xi_0), \quad (13.26)$$

where coefficient a is determined by one of conditions in Eq. 13.25. For example, the referencing of the gradient function $\bar{y}(\xi)$ to the point $\bar{y} = 0$ yields

$$a = \frac{1}{G} \left(\frac{1}{\xi_0} - \xi_0 \right). \quad (13.27)$$

Additionally, the condition $\bar{y}(\xi = \xi_1) = 1$ should be satisfied, allowing us to write

$$a(\xi_1 - \xi_0) = 1. \quad (13.28)$$

The equalities (13.27) and (13.28) form a system of equations in unknowns ξ_0 , ξ_1 , and a . To find them, we need an additional condition, which can be derived from the mass balance equation. Let V be the volume of the frustrum of cone (Fig. 13.5). Now $Q_w t = \phi V$. Simple geometric constructions allow us to find an analytic expression for the function $V = V(r_0, r_1, m)$. Passing to dimensionless variables, we obtain

$$\xi_0^2 + \xi_0 \xi_1 + \xi_1^2 = 3. \quad (13.29)$$

The same relationship can be derived from the evident integral equality:

$$1 = \xi_1^2 + 2 \int_{\xi_1}^{\xi_0} \bar{y} \xi d\xi, \quad (13.30)$$

where the integration function is determined at $\bar{y} = \bar{y}(\xi)$ Eq. 13.26, considering Eq. 13.28.

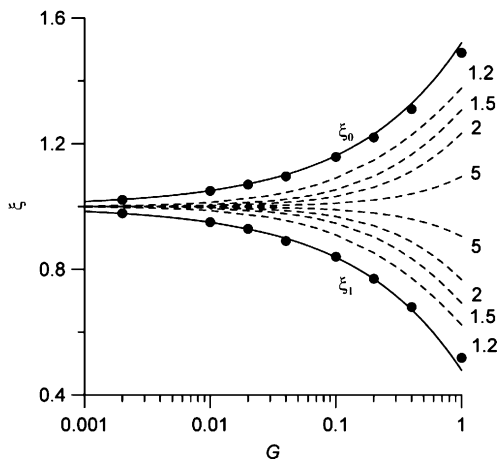
Solving simultaneously Eqs. 13.27–13.29, we come to the equation that gives us the coordinate of the frontal point:

$$\frac{2G}{1/\xi_0 - \xi_0} = \sqrt{12 - 3\xi_0^2} - 3\xi_0. \quad (13.31)$$

Accordingly, for ξ_1 we have

$$\xi_1 = \frac{-\xi_0 + \sqrt{12 - 3\xi_0^2}}{2}. \quad (13.31a)$$

Fig. 13.6 Plots of functions $\xi_0 = f(G, \bar{\mu})$ and $\xi_1 = f(G, \bar{\mu})$. The *full lines* are for $\bar{\mu} = 1$; the *dashed lines* are for $\bar{\mu} > 1$ (numbers at curves); circles show a numerical solution of Eqs. 13.41a, 13.41b with $\bar{\mu} = 1$ (Charnyi 1963)



The comparison of calculations by Eq. 13.31 with a numerical solution of the differential Eq. 13.23, (Fig. 13.6), shows that the accuracy of estimate of coordinate ξ_0 is acceptable within the range $G < 1$ (the error does not exceed 2%). The coordinate ξ_1 is better determined by the simple relationship:

$$\xi_1 = 2 - \xi_0. \quad (13.31b)$$

An approximate expression for coordinate points ξ_0 and ξ_1 can be derived from Eqs. 13.27 and 13.28, assuming $\xi_1 = 1/\xi_0$:

$$\xi_0 = \frac{\sqrt{G}}{2} (1 + \sqrt{1 + 4G^{-1}}) = \frac{1}{\xi_1}. \quad (13.32)$$

It can be easily seen that when $G \ll 1$

$$\xi_1^2 \rightarrow \xi_0^2 \approx 1, \quad (13.32a)$$

i.e., we come to the simple balance formula $Q_w t = \pi r^* 2 m \phi$ (t is the time during which solution was pumped into the aquifer with the rate of Q_w , $r^* = r_0 = r_1$ is the coordinate of the front of the displacing fluid separated from the displaced fluid by a vertical interface).

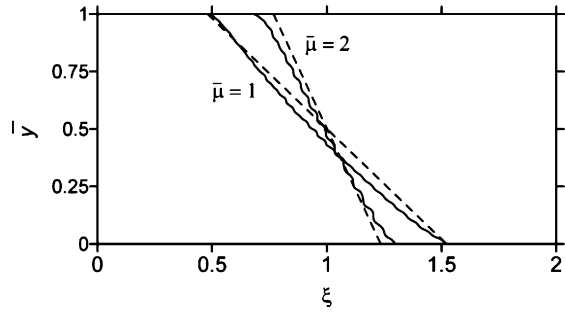
The length of the projection of the contact onto the horizontal plane in absolute values is

$$\Delta r_\rho = r_0 - r_1 = \left(\xi_0 - \frac{1}{\xi_0} \right) r^*, \quad (13.32b)$$

i.e., $\Delta r_\rho \sim \sqrt{t}$ as was the case with the rectilinear problem (see 13.1.1), since $r^* = \sqrt{Q_w t / \pi m \phi}$. When $G < 0.2$ (as is typical of most practical problems),

$$\Delta r_\rho = \sqrt{G} r^*. \quad (13.32c)$$

Fig. 13.7 To the assessment of the contribution of viscosity difference between displaced and displacement fluids to the character of deformation of their interface in an axial-symmetric flow. The *dashed line* is for an analytical solution, and the *full line* is for solution on the code TOUGH2/T2VOC. $G = 1$



Comparing Eq. 13.32c with the relationships obtained for linear flows (see Sects. 13.1.1.2–13.1.1.4) with effective specific yield, $Q = Q_w/\pi m$, we come to the relationship $\Delta r_p = \sqrt{2}\Delta x_p$.

Similar approach can be used to construct solutions taking into account the viscosity difference between the displacing and displaced fluids. In this case, as it follows from Eq. 13.22,

$$\left. \frac{d\bar{y}}{d\xi} \right|_{\bar{y}=1} = -\frac{1}{G} \left(\frac{\bar{\mu}}{\xi_1} - \frac{\xi_1}{\bar{\mu}} \right). \quad (13.33)$$

The joint solution of Eqs. 13.28, 13.29, and 13.33 makes it possible to assess the contribution of viscous resistance forces to the formation of the displacement profile of fluids with different physical properties (Fig. 13.7).

It can be seen that an increase in viscosity of the displacing fluid (when $\bar{\mu} = \mu_1/\mu_2 > 1$) contributes to the suppression of the gravity factor (Fig. 13.7): the slope of the interface between fluids increases, and the characteristic frontal points ξ_0 and ξ_1 approach each other. Analytical estimates in this range of parameters are in agreement with numerical modeling results (Fig. 13.7). These results suggest a linear character of the interface. The role of viscosity becomes critical when light, high-mobility fluids move in an aquifer (e.g., CO_2 in a supercritical state, when $\bar{\mu} \ll 1$).

13.1.2.2 Unconfined Displacement

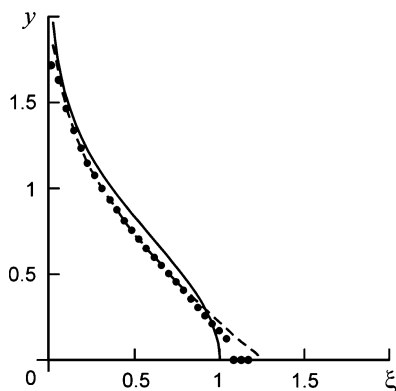
Brine well-disposal with low discharge rate results in fluid spreading on the aquifer bottom below the aquifer top, i.e., the upper part of the brine cone does not reach the aquifer top. Under Dupuit–Forchheimer assumption, the flow can be described by the equation

$$Q_w = -2\pi \frac{K}{\mu} y r \frac{dP}{dr}, \quad \mu = \mu_1 = \mu_2. \quad (13.34)$$

Suppose that an approximate hydrostatic relationship

$$\frac{dP}{dr} = \Delta \rho g \frac{dy}{dr} \quad (\Delta \rho = \rho_1 - \rho_2) \quad (13.34a)$$

Fig. 13.8 Comparison of the analytical (Eq. 13.35, *solid line*) and simulated results, code TOUGH2/T2VOC (*dashed line*, saturation equals 0.5) and code DENSFLOW (*dots*), for interface elevation



is valid in any point of the fluid–fluid interface. Integrating (13.34) with (13.34a) yields

$$\bar{y}^2 = \ln \frac{\xi_0(t)}{\xi}, \quad (13.35)$$

$$\bar{y} = \frac{y}{z_0}, \quad \xi = \frac{r}{z_0}, \quad \xi_0(t) = \frac{r_0(t)}{z_0}, \quad z_0 = \sqrt{\frac{Q_w}{\pi k \Delta \rho}}, \quad (13.35a)$$

z_0 is a scale parameter determining the brine cone rise during brine well-disposal; ξ_0 is a dimensionless “radius of influence”, characterizing, by analogy with the previous problem, the displacement velocity of saltwater tongue, $r_0(t)$, over the aquifer bottom; other denotations remain unchanged.

To find the function $\xi_0(t)$, we compose the balance equation:

$$Q_w t = \int_0^{r_0} 2\pi \phi r y dr, \quad \text{or} \quad Q_w t = 2\pi \phi z_0^3 \xi_0^2 \int_0^1 \xi' \bar{y}(\xi') d\xi', \quad \bar{y}(\xi') = \sqrt{\ln(1/\xi')}. \quad (13.36)$$

The definite integral in Eq 13.36 is equal to $\sim 1/\pi$. Thus, we have:

$$\xi_0 = \sqrt{\frac{Q_w t}{2\pi \phi z_0^3}}. \quad (13.37)$$

The comparison of the approximate solution Eq. 13.35, which, considering the character of dependences Eqs. 13.35a and 13.37 have a “self-similar” form, with independent model estimates (Fig. 13.8) shows that calculations by Eq. 13.35 yield a faster displacement of the interface in the middle part of the flow along with a small underestimation of the range of influence. This difference is not of great importance for practical calculations. The solution is convenient for estimating the major factors governing the dynamics of the process of freshwater displacement by saltwater poured into a well under unconfined regime.

13.2 Application of Two-Phase Flow Approach for Brine Transport in Porous Media Description

The model approach is based on an original and, to some extent, paradoxical idea that the two-phase flow theory can be used to describe the migration of brines (Konyukhov et al. 1998; Konyukhov et al. 2005). Fresh water and salt-saturated brine are regarded as independent liquid phases (coexisting in an elementary volume of the porous medium), whose flow is described by generalized Darcy law. The function of saturation of this volume with the brine, $S_1 \equiv S$, is identified with its relative content of dissolved salts, $\bar{C}_1$. Clearly, this model is an extreme idealization of the process since the assumption that the flows of fluids in pores are separate is a rough approximation because of the effects of molecular-diffusion and hydrodynamic-dispersion mixing, resulting in rapid leveling of the concentration profile and fluid properties at the pore level. Nevertheless, in some cases, the two-phase model may be preferred to conventional advection–dispersion models of variable-density flows.

13.2.1 Physical and Mathematical Basis

It is proposed to consider the displacement of one electrolyte salt solution by another as a process described by a saturation function, S , characterizing the share of pores occupied by a brine with salt concentration C_1 and density ρ_1 in an elementary volume. The brine is assumed not to mix with the second solution (fresh water with characteristics C_2 and ρ_2), so that the degree of saturation with this solution of the elementary volume is $1 - S$. Under such assumptions, each solution can be regarded as an independent phase.

A major advantage of this model is the possibility to effectively describe the jet-type penetration of a denser displacing fluid into a domain originally occupied by lighter (formation) water. This type of unstable fluid–fluid interface, named *fingering*, appear, for example, when the specific discharge of brine leakage through the bottom of a surface basin, q_n , is comparable with the Darcy velocity of brine movement due to density contrast at the brine–freshwater interface, $\sim k\Delta\bar{p}$ (k is hydraulic conductivity, $\Delta\bar{p}$ is density gradient). Another example is the leakage of salt solutions through contacts of beds with different permeabilities (see Sect. 14.2.2).

The effects of density-induced differentiation of solutions can be described by models involving two flow characteristics for the same representative rock volume, i.e., two phase Darcy velocities $\mathbf{q}_i$ ($i = 1, 2$). In accordance with the well-developed theory of multiphase flows (Muskat 1937; Aziz and Settari 1979), the gradient Darcy law, determining the specific discharge for each phase, has the following generalized representation:

$$\mathbf{q}_i = -\frac{\mathbf{K}}{\mu_i} k_{ri} (\nabla P_i - \rho_i \mathbf{g}) \quad (i = 1, 2), \quad (13.38)$$

where P_i is pressure $[\text{ML}^{-1}\text{T}^{-2}]$, μ_i is dynamic viscosity $[\text{ML}^{-1}\text{T}^{-1}]$, ρ_i is density $[\text{ML}^{-3}]$, $\mathbf{g}$ is the vector of acceleration due to gravity $[\text{LT}^{-2}]$, $\mathbf{K}$ is the tensor of absolute rock permeability $[\text{L}^2]$, k_{ri} is the two-phase relative permeability of phase i in the two-phase system of brine (saltwater), $i = 1$, and freshwater, $i = 2$, taken as a function of the saturation $[-]$.

The two-phase flow behavior in porous media in the absence of capillary effects is determined on the basis of a saturation–relative permeability relationship, $k_{ri} - S$. Neglecting residual saturation for a low-viscosity electrolytic system one can write linear relationships

$$k_{r1} = S, \quad k_{r2} = (1 - S). \quad (13.39)$$

In the absence of capillary effects at the phase boundaries, the pressure gradients are equal, so the Eq. 13.38 with relationships (13.39) can be represented in the explicit form:

$$\mathbf{q}_1 = -\frac{\mathbf{K}}{\mu_1} S (\nabla P - \rho_1 \mathbf{g}), \quad (13.40a)$$

$$\mathbf{q}_2 = -\frac{\mathbf{K}}{\mu_2} (1 - S) (\nabla P - \rho_2 \mathbf{g}). \quad (13.40b)$$

The phase continuity equations have the form

$$\frac{\partial}{\partial t} (\phi \rho_1 S) + \nabla \cdot (\rho_1 \mathbf{q}_1) = 0, \quad (13.41a)$$

$$\frac{\partial}{\partial t} (\phi \rho_2 (1 - S)) + \nabla \cdot (\rho_2 \mathbf{q}_2) = 0. \quad (13.41b)$$

If the fluids and the porous medium are incompressible, we obtain

$$\phi \frac{\partial S}{\partial t} + \nabla \cdot \mathbf{q}_1 = 0, \quad (13.42a)$$

$$-\phi \frac{\partial S}{\partial t} + \nabla \cdot \mathbf{q}_2 = 0, \quad (13.42b)$$

or, adding the continuity equations for both phases, we obtain the generalized equation

$$\nabla \cdot (\mathbf{q}_1 + \mathbf{q}_2) = 0, \quad (13.43)$$

whence, we have the equality

$$\mathbf{q}_1 + \mathbf{q}_2 = \mathbf{q} (= \text{const}), \quad (13.44)$$

determining the total specific discharge, $\mathbf{q}$.

Eliminating ∇P from the system of Eqs. 13.40a, 13.40b, we can represent the equation for the Darcy velocity $\mathbf{q}_1$ (the first phase) as

$$\mathbf{q}_1 = f(S) \left(\mathbf{q} + \frac{\mathbf{K} k_{r2}}{\mu_2} \Delta \rho \mathbf{g} \right), \quad (13.45)$$

which is conventionally used for the analysis of immiscible-fluid flows; here $f(S) = k_{r1}/(k_{r1} + \bar{\mu} k_{r2})$ is the so-called *Buckley-Leverett function* (Charnyi 1963; Bear 1972; Barenblatt et al. 1990); $\bar{\mu} = \mu_1/\mu_2$; $\Delta\rho = \rho_1 - \rho_2$.

Now, the total specific discharge will be determined by the expression

$$\mathbf{q} = -\frac{\mathbf{K}}{\mu_2} k^* (\nabla P - \rho \mathbf{g}). \quad (13.46)$$

where $k^* = k_{r2} + k_{r1}/\bar{\mu}$, $\rho = f\rho_1 + (1-f)\rho_2$ is effective density.

The effect of viscosity difference between the phases can be neglected in the description of migration of salt solutions, i.e., $\bar{\mu} \approx 1$ ($\mu_1 = \mu_2 = \mu$). Considering that $k_{r1} = S$, $k_{r2} = (1-S)$, $k^* = 1$, $f(S) = S$, Eqs. 13.45 and 13.46 become

$$\mathbf{q}_1 = S\mathbf{q} + S(1-S)\frac{\mathbf{K}}{\mu}\Delta\rho\mathbf{g}, \quad (13.46a)$$

$$\mathbf{q} = -\frac{\mathbf{K}}{\mu}(\nabla P - \rho \mathbf{g}). \quad (13.46b)$$

13.2.2 Properties of Particular Solutions

13.2.2.1 Vertical Two-Phase Flow of Dense Fluid

Consider the piston-like fluid displacement in a vertical flow tube when a density contrast exists between displacing and displaced fluids (Fig. 13.9). The z axis is directed vertically downward (coinciding with the direction of vector $\mathbf{g}$); the source of saltwater (brine), supplying the solute to the aquifer, is the plane $z = 0$. In this case, the process is described by Eqs. 13.42a and 13.46a, transformed into

$$\phi \frac{\partial S}{\partial t} + \frac{\partial q_1}{\partial z} = 0, \quad (13.47a)$$

$$q_1 = Sq + S(1-S)k\Delta\bar{\rho}, \quad (13.47b)$$

where k is the hydraulic conductivity (in z direction), related to the permeability K by the expression $K = \mu k/\rho_2 g$; $\Delta\bar{\rho} = (\rho_1 - \rho_2)/\rho_2$ is the density gradient; hereafter $q_1 \equiv q_{z1}$, $q_2 \equiv q_{z2}$, $q \equiv q_z$ are Darcy velocities along the z axis.

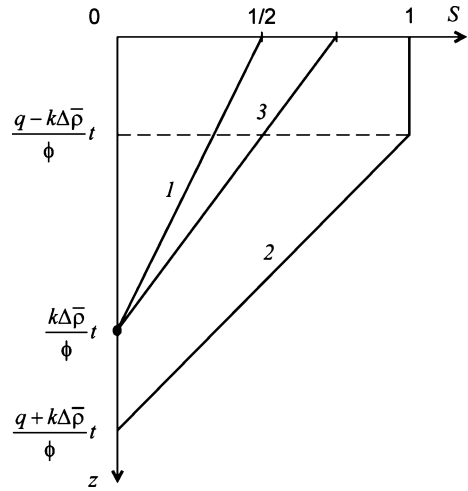
Substituting q_1 (13.47b) into (13.47a), we obtain (considering $\partial q/\partial z = 0$, see Eq. 13.43):

$$\phi \frac{\partial S}{\partial t} + (q + k\Delta\bar{\rho}(1-2S)) \frac{\partial S}{\partial z} = 0. \quad (13.48)$$

The condition that the saturation function S is constant at the boundary $z = 0$, implies that $\partial S/\partial t|_{z=0} = 0$, whence we have

$$|q + k\Delta\bar{\rho}(1-2S)|_{z=0} = 0. \quad (13.49)$$

Fig. 13.9 The distribution of $S(z)$. $1 - \bar{q} = q/k\Delta\bar{\rho} = 0$,
 $2 - \bar{q} \geq 1$, $3 - 0 < \bar{q} < 1$



Thus, we come to the conclusion

$$S(0) = \min \left[1, \frac{1}{2} \left(1 + \frac{q(0)}{k\Delta\bar{\rho}} \right) \right]. \quad (13.50)$$

The relationship (13.50) means that, if the evaluation of $S(0)$ yields a value exceeding unit, $S(0)$ is assumed to be unit. The physical meaning of Eq. 13.50 becomes clear if we consider the behavior of function $S = S(z \geq 0, t)$ with different values of the complex parameter $\bar{q} = q/k\Delta\bar{\rho}$.

Thus, in the absence of the hydrodynamic gradient of pressure at the boundary $z = 0$, i.e., when saltwater enters the bed only under the effect of density difference between the fluids in contact, $q(\bar{q}) = 0$. In this case,

$$S(0) = \frac{1}{2}. \quad (13.51)$$

Again, from Eq. 13.47b, we find the Darcy velocity of salt water at the top of the bed

$$q_1(0) = \frac{1}{4}k\Delta\bar{\rho}. \quad (13.52)$$

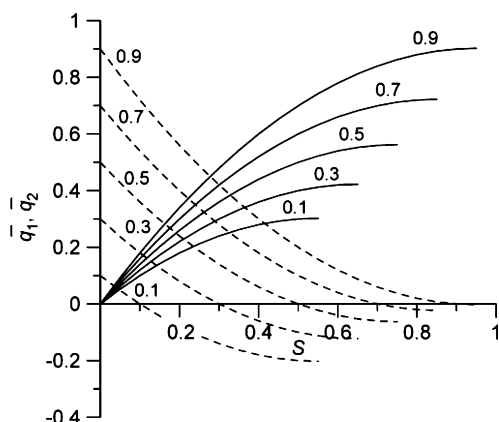
As follows from (13.48), the leading front of saturation $S = 0$ moves with the true velocity (Fig. 13.9):

$$\left. \frac{dz}{dt} \right|_{S=0} = \frac{k\Delta\bar{\rho}}{\phi}. \quad (13.53)$$

To describe the behavior of function $S(z \geq 0, t)$ for $q(0) \geq k\Delta\bar{\rho}$ (in accordance with Eq. 13.50, $S(0) = 1$), we write the continuity equation as

$$\frac{\phi}{1 + (k\Delta\bar{\rho}/q)(1 - 2S)} \frac{\partial S}{\partial t} + q \frac{\partial S}{\partial z} = 0. \quad (13.54)$$

Fig. 13.10 Plots of functions (full lines) $\bar{q}_1(S)$ and (dashed lines) $\bar{q}_2(S)$ for vertical migration of salt solution. Numbers at curves are the values of parameter $\bar{q} = q/k\Delta\bar{\rho}$



Downward displacement velocities of the interfaces $S = 0$ и $S = 1$ (Fig. 13.9) are equal

$$\left. \frac{dz}{dt} \right|_{S=0} = \frac{q + k\Delta\bar{\rho}}{\phi}, \quad \left. \frac{dz}{dt} \right|_{S=1} = \frac{q - k\Delta\bar{\rho}}{\phi}. \quad (13.55)$$

Constructing a solute balance equation for a flow tube

$$1 \, q_1(z=0)t = 1 \, \frac{q - k\Delta\bar{\rho}}{\phi} \phi t + \frac{1}{2} 1 \left(\frac{q + k\Delta\bar{\rho}}{\phi} - \frac{q - k\Delta\bar{\rho}}{\phi} \right) \phi t, \quad (13.56)$$

we obtain the equality of velocities, $q_1(z=0) = q = \text{const}$. The left part in Eq. 13.56 is the amount of salt (in the units of saturation) that have entered the bed through the inlet boundary ($z = 0$) during time t , and the right part is the amount of salt in the bed at time t . From here we have $q_2 = 0$, i.e., there is no motion of the displaced fluid.

When $0 \leq q(0) < k\Delta\bar{\rho}$, the saturation $S(0)$ varies within the range $1/2 \leq S(0) < 1$ and is determined by the general formula (13.50). We have

$$q_1(0) = \frac{q}{2} + \frac{q^2}{4k\Delta\bar{\rho}} + \frac{k\Delta\bar{\rho}}{4}. \quad (13.57)$$

Whence it follows that for any q in the range under consideration, the Darcy velocity of brine, q_1 , is greater than q ($q_1(0) > q$), i.e., the salt flux that forms due to density difference (free advection) exceeds the value of total flux at the boundary $z = 0$. Such relation can exist only if $q_2 < 0$, i.e., when the displaced solution moves in the direction *opposite* to the positive direction of the z axis. That is why, the condition of mass conservation implies $S(0) \leq 1$ (see Eq. 13.50).

Next, it can be shown that in the domain $z > 0$, at some distance from the inlet boundary, the flux of the displaced water q_2 changes its direction. Figure 13.10 gives the results of calculations by formula (13.47b) with different $\bar{q} = q/k\Delta\bar{\rho}$. It can be

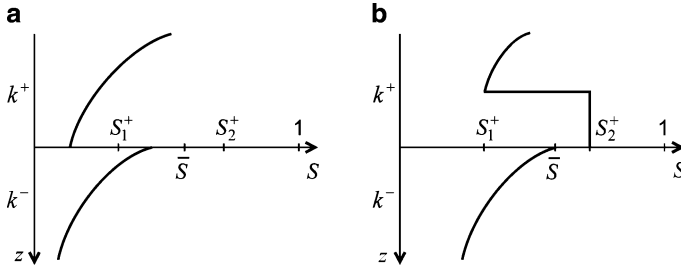
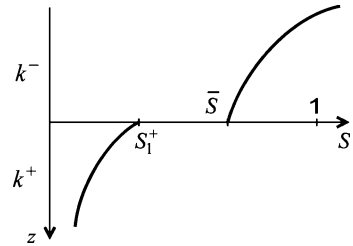


Fig. 13.11 Formation of fronts of saturation, S , near the interface between layers with different permeability ($k^+ > k^-$). (a) The initial stage of the process ($S^+ < S_1^+ < S_2^+$, $S^- < \bar{S}$); (b) the formation of a saturation jump in the top layer ($S^+ = S_2^+$, $S^- = \bar{S}$)

Fig. 13.12 Front of saturation, S , near the interface between layers ($k^+ > k^-$) during desalinization ($S^-(t=0) = 1$) of the top (low-permeability) layer ($S^+ = S_1^+$, $S^- = \bar{S}$)



clearly seen that the function $\bar{q}_2 = q_2/k\Delta\bar{p}$ ($\bar{q}_2 = \bar{q} - \bar{q}_1$) changes its sign in the point $S = \bar{q}$, i.e., at the leading front of pollution, the salt solution and water move in the same direction.

Thus, the proposed mathematical formalization of the process describes the phenomenon of mutual penetration (in the form of jet flows) of jointly moving fluids; this process cannot be correctly described by the conventional model of advection–dispersion type.

13.2.2.2 Saturation at Layer Interfaces and Saturation Jumps

Two conjugation conditions should hold at interfaces between layers with different permeability (Figs. 13.11 and 13.12): the continuity of pressure, P , and the continuity of normal fluxes of fluid components, q_n and $q_{1,n}$. The mathematical representation of this condition is as follows (Konyukhov et al. 2005):

$$P^+ = P^-, \quad q_n^+ = q_n^- = q_n, \quad q_{1,n}^+ = q_{1,n}^-; \quad (13.58)$$

the superscripts “+” and “−” correspond to the values of functions near the interface between layers with permeability k^+ and k^- ; $\vec{n}$ is the normal to the interface. The examination of the effects that appear when a saltwater flow crosses a boundary of this type is based on the following analytical constructions (Konyukhov et al. 1998).

The expression (13.58) for components $q_{1,n}^+$ and $q_{1,n}^-$ in the case of an inclined interface can be written as

$$\begin{aligned} q_{1,n}^+ &= S^+ q_n + S^+ (1 - S^+) k^+ \Delta \bar{\rho} \cos \alpha, \\ q_{1,n}^- &= S^- q_n + S^- (1 - S^-) k^- \Delta \bar{\rho} \cos \alpha, \end{aligned} \quad (13.59)$$

where $k^+ = K^+ \rho_1 g / \mu$ and $k^- = K^- \rho_1 g / \mu$ are the hydraulic conductivities of the layers; α is the slope of layer interface; $\Delta \bar{\rho} = (\rho_1 - \rho_2) / \rho_2$.

From the condition of equality of the normal components $q_{1,n}^+$ and $q_{1,n}^-$ (see 13.58), we have:

$$(S^+ - S^-) q_n = \Delta \bar{\rho} \cos \alpha (k^+ \psi^+ - k^- \psi^-), \quad (13.60)$$

where $\psi^+ = S^+ (1 - S^+)$, $\psi^- = S^- (1 - S^-)$.

The latter equality gives the following properties of function S :

1. when $\alpha \neq \pi/2$, $S^+ \neq S^-$, i.e., the saturation function has a discontinuity at the interface between layers;
2. if one of the layers is impermeable (e.g., $k^- = 0$), the relationship (13.60), where in this case, $q_n = 0$, gives $\psi^+ = 0$; this is possible only when $S = 0$ or $S = 1$, i.e., only water alone or brine alone can occur at the impermeable boundary, whence it follows that as the saturation front with any $S > 0$ reaches the interface between layers, the saturation S instantaneously becomes equal to unit.

Studying the properties of function S , resulting from a discontinuity in permeability, shows that when the domain with higher permeability (from the side of which the vertical downward salt flow moves) overlays the less permeable domain, the saturation S^- starts increasing on the side of domain $k = k^-$. The saturation S^- increases until the attainment of the velocity $q_{1,n} = q_{1,n}^-$, which has the maximal possible value $q_{1,\max}^-$. The value of $\bar{S}$ can be found from the second equation (13.59) in the point of maximum of function $q_{1,n}^- : \partial q_{1,n}^- / \partial S(\bar{S}) = 0$, whence

$$\bar{S} = \min \left[1, \frac{1}{2} \left(1 + \frac{q_n}{k^- \Delta \bar{\rho} \cos \alpha} \right) \right]. \quad (13.61)$$

Now, $q_{1,\max}^- = \bar{S} q_n + \bar{S} (1 - \bar{S}) k^- \Delta \bar{\rho} \cos \alpha$.

Flow conjugation (continuity) condition $q_{1,n}^+(S^+) = q_{1,\max}^-$ allows us to substitute $q_{1,\max}^-$ into the first equation (13.59) to obtain

$$q_{1,\max}^- = S^+ q_n + S^+ (1 - S^+) k^+ \Delta \bar{\rho} \cos \alpha; \quad (13.62)$$

its roots are

$$S_{1,2}^+ = \frac{1}{2} \left(1 + \frac{q_n}{A} \pm \sqrt{\left(1 + \frac{q_n}{A} \right)^2 - \frac{4q_{1,\max}^-}{A}} \right) \quad (13.63)$$

($A = k^+ \Delta \bar{\rho} \cos \alpha$). Since function S can take on values only in the interval $[0, 1]$, we have

$$S_1^+ = \frac{1}{2} \left(1 + \frac{q_n}{A} - \sqrt{\left(1 + \frac{q_n}{A} \right)^2 - \frac{4q_{1\max}^-}{A}} \right), \quad (13.64a)$$

$$S_2^+ = \min \left[1, \frac{1}{2} \left(1 + \frac{q_n}{A} + \sqrt{\left(1 + \frac{q_n}{A} \right)^2 - \frac{4q_{1\max}^-}{A}} \right) \right]. \quad (13.64b)$$

The relationship (13.64b) means that when S_2^+ value obtained from (13.64b) yields $S_2^+ > 1$, its value is assumed to be unit.

It is easy to show that when $S_1^+ < S^+ < S_2^+$ the velocity $q_{1,n}^+(S^+)$ is always greater than $q_{1\max}^-$, i.e., on the interface between the layers, S^+ cannot take on values from the segment $[S_1^+, S_2^+]$. From here it follows that if the saturation in the flow reaching the interface between layers increases, then, at the moment when S^+ reaches the value of S_1^+ , the saturation will jump to S_2^+ and a jump S_2^+ , will appear moving upwards (Konyukhov et al. 1998).

In another model situation, when a layer with higher permeability k^+ underlies a layer with lower permeability k^- (which at the initial moment contains salt water, Fig. 13.12), the equilibrium $S^- = \bar{S}$ (which corresponds to the velocity $q_{1\max}^-$ on the floor of the top layer), which is attained at saturation of the top layer, and $S^+ = S_1^+$, will persist until a jump S^+ , “reflected” from the floor of the high-permeability layer, arrives from below.

The formulation of two-phase flow problem considered above and the approaches to the description of the behavior of saturation functions were used to construct numerical models describing fluid flow in stratified systems (Konyukhov et al. 1998; Konyukhov et al. 2005; see also Sect. 14.2.2).

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Chapter 14

Studying Subsurface Density-Induced Phenomena Using Numerical Modeling

This chapter examines the influence of density-induced flow phenomena on solute transport in hypothetical groundwater systems taking into account different scenarios of leakage of industrial waste from surface reservoirs, as well as a scenario of upward saltwater movement from a deeper saltwater zone into the freshwater zone in response to pumping into a well using different modeling technique. Numerical modeling emerged here as one of the primary tools used to understand the most important physical processes that occur in systems containing mobile freshwater–saltwater interface. The major difficulties of density-induced subsurface transport simulation are due to the fact that the density of the water and the concentrations of chemical species dissolved in the water can vary substantially throughout the modeled area, affecting the flow pattern, and the latter, in turn, affects the change in concentration field. Thus, the flow and transport problems are coupled.

The migration of dense pollutants in aquifers has its specific features. Here are some of them.

1. If the aquifer contains fresh water, then the density difference between the waste discharged from a surface reservoir and the ambient water can cause the plume to sink towards the bottom of the aquifer. The dominating role of the gravitational component of saltwater flow, concentrated near the aquifer bottom, results in that the slope of this bottom, when its values exceed the hydrodynamic gradients of stratal water, becomes a dominating factor (other conditions being the same) determining the direction of expansion of dense solution intrusion (Dorgarten and Tsang 1991; Rumynin et al. 2002b). Under some conditions, the dense-solution lens, lying on an inclined aquiclude, can stay in dynamic equilibrium. Clearly, this equilibrium persists while the condition $I_f/I_s \approx \Delta\bar{\rho}$ is satisfied (here, I_f is groundwater head gradient directed against the dip of the impermeable bottom of the aquifer, I_s is bottom dip gradient).
2. When dense solutions enter an aquifer from a surface basin, the hydrodynamics of the regional groundwater flow may be affected: the intrusion of dense water near the bottom of the aquifer decreases the freshwater profile and consequently the effective transmissivity of the aquifer is lowered. A kind of hydrodynamic barrier forms in this case, hampering the natural groundwater flow and sometimes even causing it to change its direction.

3. The mechanism of dense solution migration from the bed of a surface basin to aquifer bottom also has its peculiar features: dense-water intrusion has the form of separate fingers, rather than a continuous flow, even when the permeability distribution over the aquifer depth is uniform.
4. The processes of density-induced advection in stratified rock formations are especially complicated. Under such conditions, the density difference between liquids facilitates mass exchange between layers, requiring significant changes in the ideas of the rate and direction of the liquid cross-flow in groundwater systems.
5. The process of migration of pollutant components in dense solutions also becomes very sensitive to the profile anisotropy in hydraulic conductivity.

14.1 On Physical Approaches to Mathematical Programming Formalism

If the salinity of the contaminant plume is much different from that of the pristine aquifer, the simulations must include the effects of density and viscosity variations. A review of the existing approaches to the simulation of density-induced transport and numerical simulators (codes) that have been developed over the past decades for coupled flow and transport modeling is provided by [Sorek and Pinder \(1999\)](#), [Zheng and Bennett \(2002\)](#), [Bear and Cheng \(2010\)](#) and others.

Two approaches are generally used to simulate freshwater–saltwater interactions ([Bear 1979](#)). In the first approach, the freshwater and saltwater are two immiscible fluids and are separated by a well-defined, sharp interface; this approach may incorporate the Ghyben–Herzberg approximation. In the second approach, the freshwater and saltwater are considered as a single fluid having a spatially and temporary variable salt concentration that influences the fluid's density; this approach is referred to as fully miscible groundwater flow and density-dependent solute-transport modeling. Studying variable-density flows may be based on two-phase groundwater flow models ([Konyukhov et al. 1998, 2005](#); see Sect. 13.2.2).

The first approach yields good results in the analysis of practically important situations involving the estimation of the horizontal development of pollution plumes, when their horizontal size is much greater than their thickness. Physico-mathematical formalization and numerical description of the process can be found, for example, in the computer code DENSFLOW ([Rumynin and Konosavsky 1999](#)).

DENSFLOW is a sharp-interface numerical simulator, which simulates the migration of freshwater and saltwater as two immiscible fluids in a single-layer (confined or unconfined) aquifer and averages the flow properties of the aquifer over the vertical; thus, the process is considered in a quasi-three-dimensional formulation. The numerical approach is aimed at predicting the thickness of saltwater wedge in the vertical profile (Fig. 14.1).

For each flow domain, the equation of continuity may be integrated over the vertical coordinate, reducing the determination of the position of the interface to

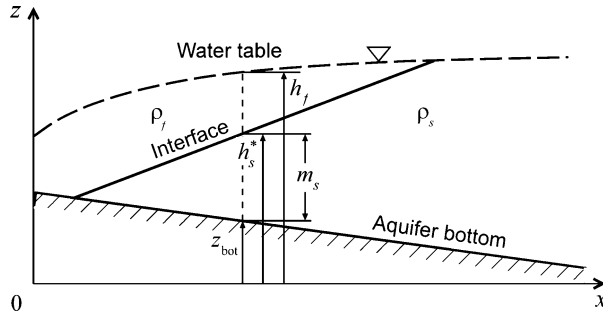


Fig. 14.1 Conceptual diagram showing the two-liquid interface characteristics used in DENS-FLOW simulator algorithm

a problem of two dimensions, x and y (Gemitzi and Tolikas 2004). Such process decoupling occurs only within the internal numerical procedure with subsequent coupling of solutions obtained for the two domains.

The flow equation in the saltwater domain is solved in terms of equivalent freshwater head (Shestakov 1995; Pozdniakov 1996)

$$h_s = h_f - h_s^* + m_s \bar{\rho} + z_{\text{bot}}; \quad (14.1)$$

here h_s is the reduced hydraulic head related to the saltwater domain; h_f is freshwater hydraulic head; h_s^* is the elevation of the fresh–saltwater interface; z_{bot} is the elevation of the aquifer bottom; m_s is the current (in modeling block) thickness of the saltwater wedge; $\bar{\rho} = \rho_s / \rho_f$. Inverse calculation at the moment of output to the external cycle is based on the Ghyben–Herzberg approximation

$$m_s = (h_s - h_f) / (\bar{\rho} - 1). \quad (14.1a)$$

Corrections are introduced to the calculated heads to account for changes in the hypsometry of aquifer bottom.

For unconfined flow, the vertically integrated equations of freshwater and saltwater flow are, respectively:

$$\begin{aligned} S_{yf} \frac{\partial h_f}{\partial t} + w_f &= \frac{\partial}{\partial x} \left[k_f(x, y) (h_f - h_s^*) \frac{\partial h_f}{\partial x} \right] + \frac{\partial}{\partial y} \left[k_f(x, y) (h_f - h_s^*) \frac{\partial h_f}{\partial y} \right], \\ S_{ys} \frac{\partial h_s}{\partial t} + w_s &= \frac{\partial}{\partial x} \left[k_s(x, y) (h_s^* - z_{\text{bot}}) \frac{\partial h_s}{\partial x} \right] + \frac{\partial}{\partial y} \left[k_s(x, y) (h_s^* - z_{\text{bot}}) \frac{\partial h_s}{\partial y} \right], \end{aligned} \quad (14.2a)$$

where k_f and k_s are the hydraulic conductivities of freshwater and saltwater domains; S_{yf} and S_{ys} are the specific yield for freshwater and saltwater domains; w_f and w_s are the source/sink terms for fresh and saltwater, respectively; h_s^* is the actual hydraulic head for saltwater, with $h_s^* = z_{\text{bot}}$, $h_f - h_s^* \equiv h_f - z_{\text{bot}}$.

For a confined flow, the system of Eqs. 14.1 b is reduced to

$$\begin{aligned}\eta_f^* \frac{\partial h_f}{\partial t} + w_f &= \frac{\partial}{\partial x} \left[k_f(x, y) \frac{\partial h_f}{\partial x} \right] + \frac{\partial}{\partial y} \left[k_f(x, y) \frac{\partial h_f}{\partial y} \right], \\ \eta_s^* \frac{\partial h_s}{\partial t} + w_s &= \frac{\partial}{\partial x} \left[k_s(x, y) \frac{\partial h_s}{\partial x} \right] + \frac{\partial}{\partial y} \left[k_s(x, y) \frac{\partial h_s}{\partial y} \right],\end{aligned}\quad (14.2b)$$

where η_f^* and η_s^* are the specific storage for freshwater and saltwater domains [L^{-1}].

The brine is an impermeable boundary of the second type for the light liquid; therefore, all flow resistance parameters are corrected at each time step to account for the varying thickness of the watered zone. For the dense liquid, the freshwater overlying its tongue creates additional pressure on the freshwater–saltwater interface, i.e., the distribution of heads in the problem of dense-liquid flow is governed not only by the thickness of the tongue itself, but also by the thickness of the overlying freshwater layer. Such approach, irrespective of other features of the flow, requires the use of an iteration calculation algorithm.

In addition to the above said, the program DENSFLOW allows for (1) variable space and time steps; (2) separate input of hydraulic conductivity parameters, additional sources (sinks) functioning in the freshwater and saltwater domains; (3) boundary conditions of the first, second, and third types (invariable over time); (4) horizontal heterogeneity of hydraulic conductivity distribution; (5) hypsometry of the aquifer's top and bottom.

The calculation algorithm is based on the point iteration technique with over-relaxation (SOR). Test calculations have shown that the iteration process convergence control based on the head discrepancy alone is not enough; therefore, the balance discrepancy of the model should be checked in all grid-blocks because of a strong sensitivity of calculation to the position of freshwater–saltwater interface. The admissible total imbalance of the sharp-interface model is determined by the user for freshwater and brine separately.

A large amount of theoretical work has been done to develop a *second approach*, namely, density-dependent miscible-fluid flow and transport modeling. A lot of numerical models have been developed, among them are such well-know codes as TOUGH2 (Pruess 1987; 1991a, b; Pruess et al. 1999; Oldenburg and Pruess 1993, 1995; Pruess 2004), SUTRA (Voss and Provost 2002), HST3D (Kipp 1997), METROPOL-3 (Leijnse and Oostrom 1995), FEMWATER (Yeh et al. 1994), MOCDENS3D (Essink 1998), SEAWAT-2000 (Guo and Langevin 2002), GEON3D (Zinin et al. 2003), MIG2 (Kuvaev 1995). These models are modular computer programs that simulate fluid movement and the transport of dissolved substances (some of codes have options to simulate energy transport) in the subsurface. The results of simulation of saltwater movement show distributions of fluid pressures, dissolved solids concentrations, and the magnitude and direction of fluid velocities as they vary over time. Almost all values of aquifer properties that are entered into the model may vary throughout the simulated section. Sources and boundary conditions may vary over time. The models have been applied to real field data and found to give favorable results.

The more common mathematical models of brine transport in porous media are based on the works of [Bear \(1972\)](#), [Lake \(1989\)](#) and [Bear and Cheng \(2010\)](#). The governing equations for numerical models consist of mass conservation equations and Darcy's law for fluid flow. Pressure and water density (total solute concentration) are the dependent variables.

Most numerical algorithms used to model single-phase variable-density flow are designed for solving equations written in the differential form. Thus, the conservation of mass of components in the fluid phase given by [Lake \(1989\)](#) and [Chen et al. \(2006\)](#) in more common differential formulation is as follows

$$\frac{\partial \rho \omega_i}{\partial t} + \frac{\partial}{\partial t} [(1 - \phi) \rho_s \omega_{is}] + \nabla \cdot [\rho \omega_i \mathbf{v} - \mathbf{D}_i \nabla \omega_i] = W_i, i = 1, 2, \dots, N_c, \quad (14.3)$$

where ϕ is the porosity; ρ and ρ_s are the densities of liquid and solid phases; ω_i and ω_{is} are the mass-fractions of the i th component in the liquid and solid phases $[-]$, related with volumetric concentrations, C_i and C_{is} , through equations $C_i = \omega_i \rho$ and $C_{is} = \omega_{is} \rho_s$, where $\sum_{i=1}^{N_c} \omega_i = 1$ and $\sum_{i=1}^{N_c} \omega_{is} = 1$ (N_c is the total number of the components in the solution); $\mathbf{D}_i$ is the diffusion–dispersion tensor, which is specified according to Eqs. 1.20 and 1.23; W_i is the source/sink term for chemical kinetics; $\mathbf{v}$ is the specific discharge (Darcy velocity) tensor which is determined by equation

$$\mathbf{v} = -\frac{\mathbf{K}}{\mu} \cdot (\nabla P - \rho \mathbf{g}) \quad (14.3a)$$

(P is the pressure, $\mathbf{K}$ is the absolute permeability of the sediment or rock, μ is the dynamic viscosity). The system of Eqs. 14.3 and 14.3a must be supplemented by an equation of mass balance of the fluid ([Chen et al. 2006](#)).

A more general approach to the mathematical formulation of the problem ([Pruess 1987, 2004](#)) is based on the consideration of the basic mass conservation equation:

$$\frac{d}{dt} \int_{V_n} M^i dV = \int_{\Gamma_n} \mathbf{J}^i \cdot \mathbf{n} d\Gamma + \int_{V_n} W^i dV, i = 1, 2, \dots, N_c. \quad (14.4)$$

The integration is carried out over an arbitrary subdomain V_n of the flow system under study, which is bounded by the closed surface Γ_n ; M^i is the mass per volume of the i th labeling component,

$$M^i = \phi \rho \omega^i; \quad (14.4a)$$

$\mathbf{J}^i$ is the mass flux,

$$\mathbf{J}^i = \mathbf{v} \rho = -\mathbf{K} \frac{\rho \omega^i}{\mu} (\nabla P - \rho \mathbf{g}); \quad (14.4b)$$

W^i is the sink/source intensity; $\mathbf{n}$ is an inward normal to surface $d\Gamma_n$.

Equation 14.4 expresses the fact that the rate of change of fluid mass in V_n is equal to the net inflow across the surface of V_n , plus the net gain from fluid sources ([Pruess 2004](#)). In the analysis of some class of problems, Eq. 14.4 is also considered as an energy conservation equation, in which case the flow term contains convection and conductance components.

We can formally use Gauss theorem to transform Eq. 14.4 into a partial differential equation of the form of (14.3). However, when constructing the calculation algorithm, we can omit this procedure and use the method of “direct discretization” of the integral terms in Eq. 14.4. Such approach, named Integral Finite Difference method (IFD), is implemented in a numerical simulator TOUGH2 (Pruess 1991a, b; Pruess et al. 1999; Pruess 2004). TOUGH2 code provides for the formulation of various Equations of State (EOS) for different physical systems. In particular, EOS7 is used to describe the migration of brines, which is the purpose of this chapter.

Unfortunately, finite-difference and integral methods for solving differential equations feature high dispersion (which is practically uncontrollable during calculations), which may lead to qualitatively wrong results in studying some class of problems. Thus, when leakages of dense solutions from surface basins of industrial wastes are modeled on “coarse” grids, the matter will be “smeared” over the flow depth: the intrusion core (with salt concentration close to the boundary value) has not enough time to form, resulting in underestimation of the role of the gravitation component in the formation of saltwater plume. Therefore, the use of algorithms involving the suppression of numerical effects based on the Random Walk method (e.g., MIG2 numerical simulator) or on the method of characteristics (MOC-DENS3D) allows one to more adequately reproduce the physical process with the same grid chosen for the model domain.

There are MODFLOW-based programs currently available for simulation of density-dependent flow (Langevin and Guo 2006). MODFLOW-based codes designed to simulate variable-density flow typically solve a formulation of the groundwater flow equation in terms of equivalent freshwater head.

Finally, the use of *two-phase flow* models (see Sect. 13.2, code 2PHFLOW), allows one to study the migration of solutions with pronounced fingering effect, though with some drawbacks in process schematization (the need to a priori specify an equation to relate the phase permeability with the phase saturation and neglect the within-pore diffusion, which smoothes the interface) (Konyukhov et al. 1998; Konyukhov et al. 2005). The efficient procedures proposed by those authors for modeling the propagation of saturation jumps (see Sect. 13.2.2.2) make it possible to study various problems, which are difficult to solve by other numerical methods. Of use for this purpose also may be the module T2VOC (TOUGH2 simulator), which is designed for modeling three-phase flows in three-dimensional formulation (Falta et al. 1989, 1995).

14.2 Brine Migration in Idealized Aquifer Systems

14.2.1 Numerical Simulators' Performance Capabilities and Their Testing

It is standard practice to verify a numerical simulator (code) before applying it to practical problems. There are three requirements to be met for a numerical code to be accepted as a useful tool (Tsang and Doughty 1985). First, it must be verified against

analytical solutions to show that the governing equations of the mathematical model have been correctly programmed into the code, and the numerical solution algorithm works with adequate accuracy. Second, it must be verified against modeling results obtained for benchmark problems using previously tested numerical codes (cross-validation procedure for model selection). Third, it must be validated against experimental data in order to check that the mathematical model used properly represents the physical processes taking place.

A commonly accepted approach to testing (verification) of computer codes is the comparison of numerical calculations and analytical solutions of *benchmark problems*, considered as some standard. Thus, a common step is to turn to the classical problem of seawater intrusion into coastal aquifers (Fig. 14.2), assuming sharp interface approximation (idealistic scenario, $D = 0$, see Sect. 13.2). This configuration leads to a stationary saltwater intrusion wedge penetrating landward on the aquifer bottom.

The problem considers a vertical slice through an isotropic, homogenous and confined aquifer. A constant flux of freshwater is applied to the inland boundary, while a seaward boundary is exposed to a stationary body of higher density seawater.

Analytical relationships (Glover 1959; Henry 1959) for the description of the *stationary* phase of the process have the form of (12.17) and (12.18). The governing parameter is

$$a = \frac{1}{G}, G = \frac{k\Delta\bar{\rho}m}{Q_0} \equiv \frac{Kgm(\rho_s - \rho_f)}{\mu Q_0}, \quad (14.5)$$

which for our test example (Table 14.1) is 0.2691; here Q_0 is the discharge of freshwater flow; k is the hydraulic conductivity; m is aquifer thickness;

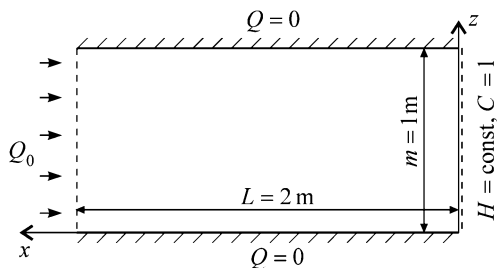
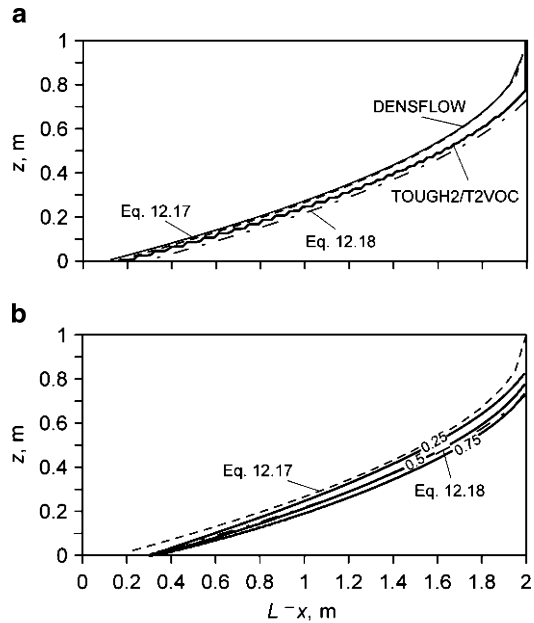


Fig. 14.2 Geometry and boundary conditions of a benchmark system

Table 14.1 Parameters and boundary conditions for the classical problem of seawater intrusion (sharp interface approach)

Model characteristics	Values
Model length/height	2 m/1 m
Initial conditions	$\bar{C} = 0$, $\rho = \rho_f = 1000 \text{ kg m}^{-3}$, $\mu = 0.001 \text{ kg m}^{-1} \text{ s}^{-1}$
Boundary conditions:	
Left side	$Q_0 = 6.6 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$, $\bar{C} = 0$, $\rho_f = 1000 \text{ kg m}^{-3}$, $\mu = 0.001 \text{ kg m}^{-1} \text{ s}^{-1}$
Right side	$P = \rho gh = \text{const}$, $\bar{C} = 1$, $\rho_s = 1025 \text{ kg m}^{-3}$, $\mu = 0.001 \text{ kg m}^{-1} \text{ s}^{-1}$
Top and bottom	$Q_0 = 0$
Permeability, K	1.10^{-9} m^2
Porosity, ϕ	0.35

Fig. 14.3 Comparison of numerical and analytical solutions for a steady-state problem of seawater intrusion in a coastal aquifer. (a) DENSFLOW ($N_x = 40$) and TOUGH2/T2VOC ($N_x = 100$, $N_z = 50$); (b) TOUGH2/EOS7 ($N_x = 200$, $N_z = 100$); N_x and N_z are the numbers of grid-blocks in x and z directions



$\Delta\bar{\rho} = (\rho_s - \rho_f)/\rho_f$ is the density gradient between liquids of equal viscosity, μ ; K is the absolute permeability; g is the acceleration of gravity. A graphical representation of solutions (12.17) and (12.18) is given in Fig. 14.3.

A numerical solution of the problem obtained by using DENSFLOW sharp-interface simulator based on Ghyben–Herzberg approximation is superimposed on the plot in Fig. 14.3a. The numerical solution almost coincides with the analytical solution, Eq. 12.17. The same plot shows a numerical solution of the problem for an effective two-phase flow (TOUGH2/T2VOC simulator, a linear relationship is specified between the saturation with respect to salt solution and the phase relative permeability), which shows a good agreement with another analytical solution, Eq. 12.18. Such results can be considered as a proof that the dynamic equilibrium in the opposite motion of two liquids (steady-state problem) can be described by an approximate hydrostatic model.

Another plot (Fig. 14.3b) illustrates a complete solution of the problem by finite-element method (TOUGH2/EOS7 code). Some smearing of the front is due to the numerical dispersion, since EOS7 modulus does not support the modeling of physical dispersion (diffusion) process. The isoline of 50% concentration (with which the position of the piston-like displacement front can be associated) is almost exactly described by solution (12.18).

Some self-similar solutions (asymptotics) can be used for additional testing of such models. Thus, the quite satisfactory agreement between numerical and analytical solutions (Barenblatt and Shestakov 1955; Barenblatt and Shestakov 1956; Polubarinova-Kochina 1962), as well as solution (13.35) of *nonsteady-state* problems of this type (in linear profile and cylindrical formulation) is illustrated by curves in Fig. 14.4. Errors in the estimates of current coordinates of the brine–water

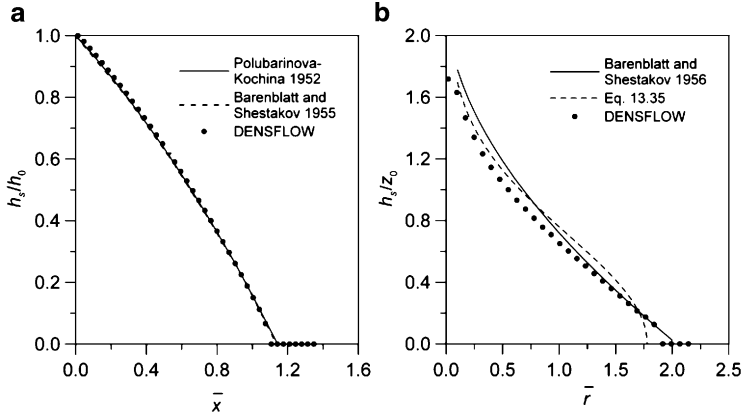


Fig. 14.4 Comparison of analytical (self-similar) and numerical (DENSFLOW) solutions of linear (a) and axially symmetrical (b) problems for a two-liquid sharp-interface displacement system. $\bar{x} = x/\sqrt{2kh_0\Delta\bar{\rho}t/\phi}$, $\bar{r} = r/\sqrt{Q_w t/2\pi z_0\phi}$, $z_0 = \sqrt{Q_w/\pi k\Delta\bar{\rho}}$. k and ϕ are hydraulic conductivity and porosity, respectively; $\Delta\bar{\rho}$ is density gradient; h_0 water column height on the boundary; h_s is the current thickness of saltwater layer; t is current time; r is radial coordinate; Q_w is the rate of water inflow into the well

interface in the median plane of the flow do not exceed 5–7%, and the same level of errors is typical of calculations of the length of saltwater intrusion.

A classical example a benchmark problem is the *Henry problem*, connected with simulation of transition (mixing) zone between two liquids in the coastal confined aquifer. Mixing is caused by diffusion processes ($D = \text{const} \neq 0$) and results in some of the salt being driven seawards by freshwater. Henry (1964) was the first to obtain a solution (numerical–analytical method) of this problem, named after him. Later, after a long discussion based on comparative analysis of various model experiments (Friend 1982; Huyakorn et al. 1987; Voss and Souza 1987; Croucher and O’Sullivan 1995; Cameo 2006; Dentz et al. 2006; Meca et al. 2007), the solution given by Henry (1964) was improved (Segol 1993; Simpson and Clement 2004). In whole, Henry problem has played a significant historical role in our understanding of seawater intrusion and examination of capability of numerical codes to simulate the density-induced transport problems.

The solution for a stationary function includes three dimensionless combined parameters:

$$\xi = \frac{L}{m}, a = \frac{1}{G}, b = \frac{D}{Q_0}. \quad (14.6)$$

The first combined parameter represents the geometry of the model domain; the second one accounts for the relative importance of buoyancy and viscous forces; and the third one quantifies the relative importance of purely advective and dispersive transport mechanisms (see also Sects. 12.2 and 13.1). A specific variant of calculated isolines of concentration $\bar{C}(x, z, t \rightarrow \infty)$ in the domain $0 \leq x \leq L$, $0 \leq z \leq b$ (Fig. 14.2) with parameters $\xi = 2$, $a = 0.263$, $b = 0.1$ (Table 14.2) is given in Fig. 14.5 (triangles on curves).

Table 14.2 Parameters and boundary conditions for the Henry problem

Model characteristics	Values
Model	
length/height	2 m/1 m
Initial conditions	$\bar{C} = 0, \quad \rho = \rho_f = 998.36 \text{ kgm}^{-3}, \quad \mu = 0.0010017 \text{ kgm}^{-1} \text{ c}^{-1}$
Boundary conditions:	
Left side	$Q_0 = 6.6 \cdot 10^{-5} \text{ m}^2 \text{ c}^{-1}, \bar{C} = 0, \quad \rho_f = 998.36 \text{ kgm}^{-3}, \mu = 0.0010017 \text{ kgm}^{-1} \text{ c}^{-1}$
Right side	$P = \rho gh = \text{const}, \bar{C} = 1, \quad \rho_s = 1025 \text{ kgm}^{-3}, \mu = 0.0010017 \text{ kgm}^{-1} \text{ c}^{-1}$
Top and bottom	$Q_0 = 0$
Permeability, K	$0.96025 \cdot 10^{-9} \text{ m}^2$
Dispersion, D	$6.59995 \cdot 10^{-6} \text{ m}^2 / \text{c}$
Porosity, ϕ	0.35

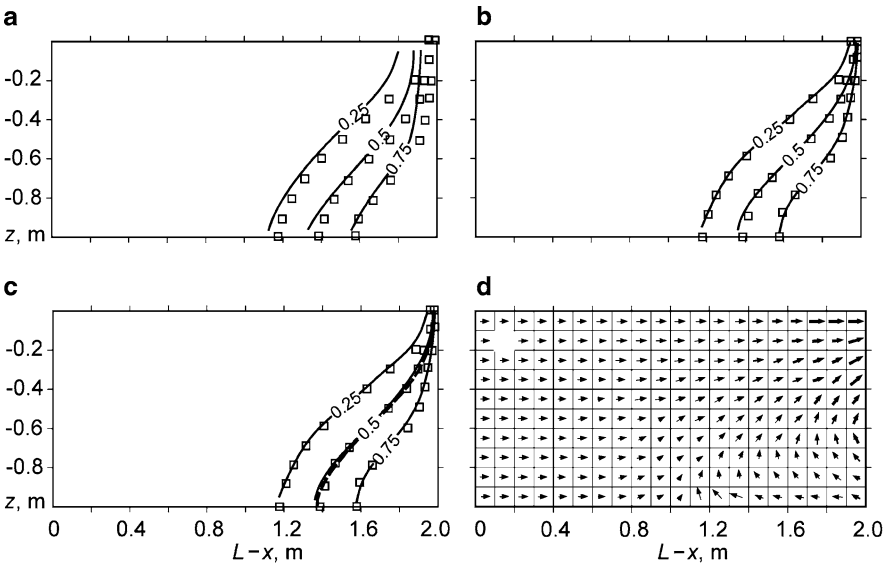


Fig. 14.5 Comparison of numerical and semi-analytical results for the Henry problem. *a, b, c* are results obtained using TOUGH2 for different variants of model domain fragmentation: **(a)** 20×10 , **(b)** 100×50 , **(c)** 160×80 ; squares are for numerical–analytical solution (Simpson and Clement 2004); **(d)** velocity field, SEAWAT-2000 solution (Langevin et al. 2003)

Comparison of the results of calculations carried out on various grids (Fig. 14.5), confirms that the fulfillment of the grid relationship $k > 5$ (where k is found from the identity $N_z = 2^{k+1} + 1$, N_z is the number of nodes in the vertical direction, and $N_z = N_x/2$, N_x is the number of nodes in the horizontal direction x) is enough (Croucher and O’Sullivan 1995) for the problem to be solved with high accuracy. In particular, it can be seen that the numerical dispersion with fine division of the domain into model blocks does not lead to any serious errors in calculated concentration distribution.

As can be seen, the results obtained by using TOUGH2 almost completely coincide with the numerical–analytical solution of the problem presented in (Simpson and Clement 2004). Additionally, a curve ($\bar{C} = 0.5$), demonstrating the solution of “network” problem by Meca et al. (2007), was plotted in Fig. 14.5c. TOUGH2-results are very close to calculations made by this method. The coordinate of maximal propagation of saltwater tongue (along the isoline of relative concentration $\bar{C} = 0.5$) against the freshwater flow is 1.372 m. The same value is estimated at 1.409 (Voss and Souza 1987), 1.400 (Segol 1993), 1.375 (Croucher and O’Sullivan 1995), 1.393 (Simpson and Clement 2004), 1.394 (SEAWAT-2000, Langevin et al. 2003), and 1.373 m (Meca et al. 2007).

Finally, Fig. 14.5d gives a flow velocity field illustrating the formation of a vertical convection cell in the system. The cell is formed by seawater that flows landward in bottom layers and disperses into the freshwater flow zone, where salt is carried out by the discharging freshwater (Cameo 2006). The cell forms because of the need to satisfy the flow continuity conditions in the contact zone between different-density liquids (the fresh and salt waters must flow in the same direction within the dispersion zone). In other words, seawater movement is caused by a combination of density-driven flow and hydrodynamic dispersion. The equilibrium assumption of Ghyben–Herzberg is not valid because seawater flux causes a loss in seawater head. Therefore, the saltwater wedge recedes with increasing dispersion.

The Henry problem has one more mathematical formalization, implying that at the landward ($x = L$) and seaward ($x = 0$) boundaries, the pressure distribution is specified to be hydrostatic (Dentz et al. 2006). The authors provide a systematic analysis of the modified Henry problem for a full range of the Peclet number, $Pe = k\Delta h_0 / \phi D \approx 1/b$ (where Δh_0 is the hydraulic head contrast between the boundaries), and the coupling parameter, $\alpha = \Delta \bar{\rho} L / \Delta h_0 \approx G$.

Overall, the examples given above show that the tested codes, which will be widely used in the further analysis, satisfactorily reproduce density-induced convection phenomena in homogeneous systems where horizontal advection is dominant.

14.2.2 *Physical Phenomena Analysis for Migration of a Brine Released from a Surface Reservoir*

14.2.2.1 *Brine Behavior in a Stratified Aquifer*

The layered structure of the aquifer and strong gravity effects, implying tightly coupled flow and transport processes, provide a stringent test of the numerical code’s ability to model the real subsurface conditions. In this connection we consider numerical solutions of two-dimensional vertical-plane problem of brine migration in a three-layer water-bearing stratum, obtained by using different software packages. The flow model section and the character of boundary conditions are schematized in Fig. 14.6. Problem formulation assumes brine input ($\rho = \rho_s = 1070 \text{ kgm}^{-3}$) with

Fig. 14.6 A conceptual model of a three-layer aquifer

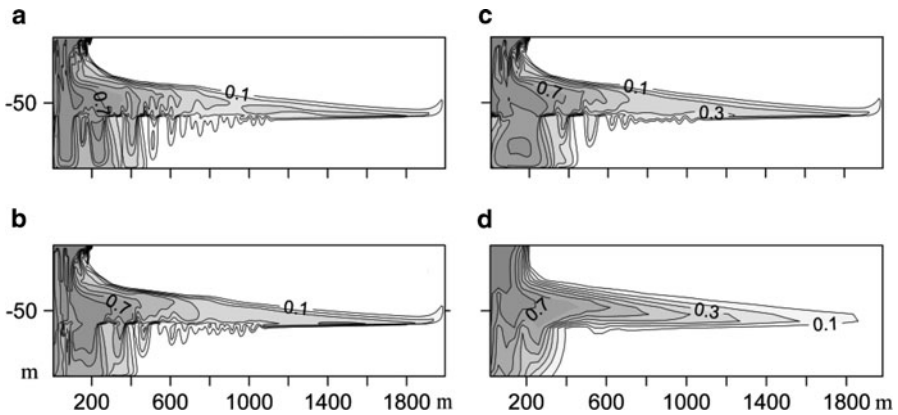
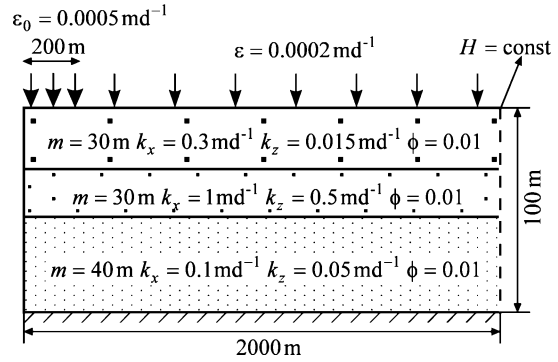


Fig. 14.7 The influence of the model domain refinement on the dense-water plume behavior in a three-layer aquifer (TOUGH2/EOS7 results). Time, $t = 3,200$ day. Numbers at curves show relative concentrations. Hereafter, the distances along axes x and z are given in meters; the vertical and horizontal dimensions of a model grid-block are (a) 5×1 m, (b) 10×0.5 m, (c) 10×1 m, (d) 40×5 m

a rate of $\varepsilon_0 = 5 \cdot 10^{-4} \text{ md}^{-1}$ from a surface basin under the effect of area-distributed freshwater ($\rho = \rho_f = 1000 \text{ kgm}^{-3}$) infiltration into a three-layer anisotropic aquifer with a rate of $\varepsilon = 2 \cdot 10^{-4} \text{ md}^{-1}$.

The numerical solutions obtained by TOUGH2/EOS7 package (Fig. 14.7), demonstrate the dynamics of plume spreading. In particular, it can be seen that, notwithstanding the presence of a high-permeability layer in the middle of the section, a considerable mass of dense water sinks to the foot of the horizon, where the hydraulic conductivity is an order of magnitude less than in the overlying layer. At the same time, it can be seen that the elevated numerical dispersion in combination with the large size of blocks results in some underestimation of the role of density gradient and hence to overestimation of the contribution of the high-permeability layer to pollutant transport.

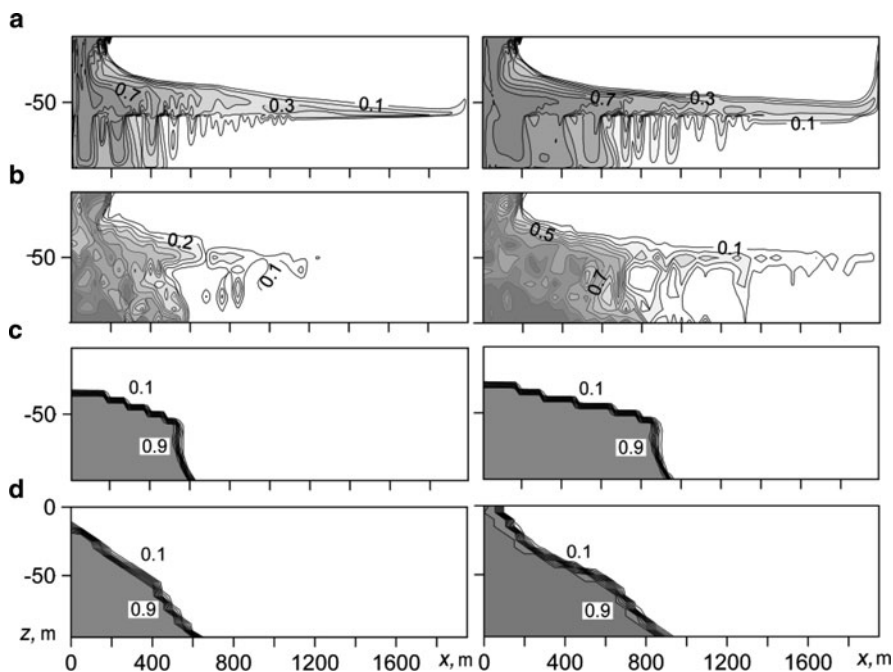


Fig. 14.8 Results of numerical modeling of brine migration in a three-layer aquifer. Figures on curves show the relative concentration. The left column: $t = 3200$ d; the right column: $t = 5200$ d. (a) – TOUGH2/EOS7 (5×1 m); (b) – MIG2 (50×10 m); (c) – TOUGH2/T2VOC (20×5 m); (d) – 2PHFLOW (50×5 m)

In the context of model approaches described here, of interest is to perform comparative analysis of results obtained from different software packages: TOUGH2 (modules EOS7 and T2VOC), MIG2, and 2PHFLOW, as applied to the same transport conditions in a three-layer strata (Fig. 14.8). As can be seen, different approaches to the physico-mathematical formalization of brine migration process (Sect. 14.1) yielded somewhat different distributions of $\bar{C}(x, z, t)$.

Extreme results were obtained by model simulation of the process using TOUGH2/EOS7 package, on the one hand, and TOUGH2/T2VOC and 2PHFLOW packages, on the other hand (Fig. 14.8). Clearly, in the modeling of the advection of mixing different-density liquids by finite-element method (TOUGH2/EOS7) (Fig. 14.8a), the effect of profile heterogeneity of the bed is maximal; though the role of advective transport along the middle layer, which has the highest permeability, may be somewhat overestimated because of errors in modeling the gravitation component ($\partial\rho/\partial z$) of flow on a coarse grid. Contrary to that, the solution of the problem assuming two-phase flow (TOUGH2/T2VOC and 2PHFLOW) (Fig. 14.8c–d) is only slightly sensitive to the profile heterogeneity, resulting in an overestimation of the role of density-induced advection along with underestimation of pollutant migration in small concentrations in the high-permeability layer.

The result obtained with MIG2 (Fig. 14.8b) package is, in a sense, intermediate, and appears to be the best describing the real distribution of function $\bar{C}(x, z, t)$.

In all variants, irrespective of the choice of the numerical scheme, the major portion of brine is concentrated in about the same model domain – the bottom part of the water-bearing stratum. Therefore, it would appear reasonable that, on the one hand, the permeability of the bottom layer plays a dominating role in the development of saltwater intrusion from the surface pollution source, and, on the other hand, the velocity of pollution transport in small concentration from the source (the left boundary) to the drainage zone (the right boundary) is determined by the transmissivity of the high-permeability (middle) layer.

14.2.2.2 Subvertical Saltwater Flows Near the Surface Basin

The problem of propagation of a dense-brine intrusion in a homogeneous confined aquifer is solved (Fig. 14.9). Constant head is specified on the left and right boundaries of the model domain; the formation of groundwater flow in the bed takes place due to the area-distributed infiltration of freshwater and the leakage of high-concentration solution (brine) from the basin.

As follows from the comparative analysis of the obtained data (Fig. 14.10), the models of two-phase flows (TOUGH2/T2VOC and 2PHFLOW numerical simulators) yielded practically equivalent results, suggesting the dominating transport of pollution near the bottom of the aquifer in the form of a rising saltwater dome. This seemingly illogical effect is due to the fact that those numerical simulators, in their limiting version, allow one to describe the rapid transport of a dense solution from the aquifer top to bottom through fingering. Since this phenomenon takes place under natural conditions as well, in this case, the models of two-phase flows have some advantages relative to dispersion models, the use of which leads to an appreciable overestimation of the size of pollution zones in the top part of the section (Figs. 14.10 and 14.11). The interface between the two liquids almost coincides with the interface, obtained from DENSFLOW (Fig. 14.10).

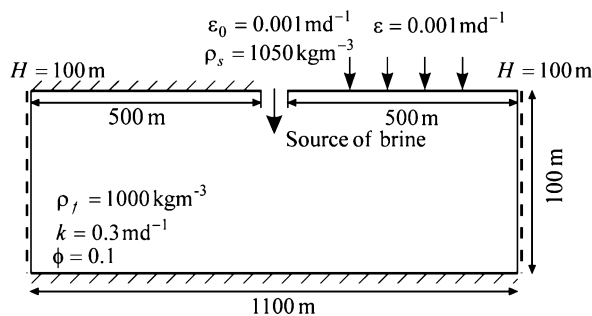


Fig. 14.9 Conceptual scheme of numerical experiment for studying variable-density surface water-groundwater interaction

Fig. 14.10 Comparison of modeling results of brine migration in a homogenous aquifer using different numerical simulators. (a) DENSFLOW ($dx = 5$ m), TOUGH2/T2VOC ($dx = 10$ m, $dz = 5$ m), 2PHFLOW ($dx = dz = 2.5$ m); (b) MOC3DD ($dx = 10$ m, $dz = 5$ m). Time, $t = 15,000$ day

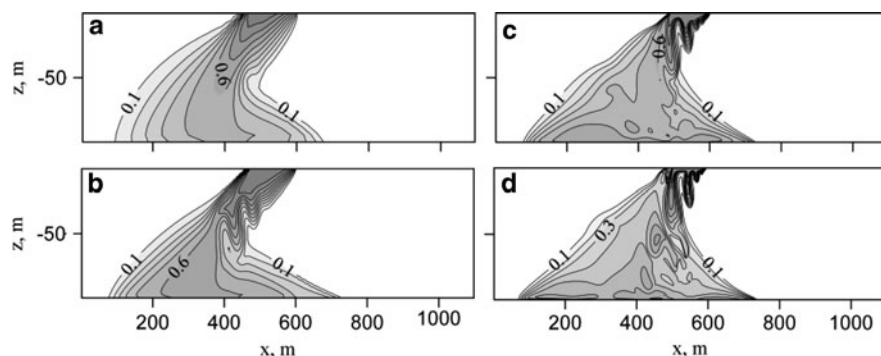
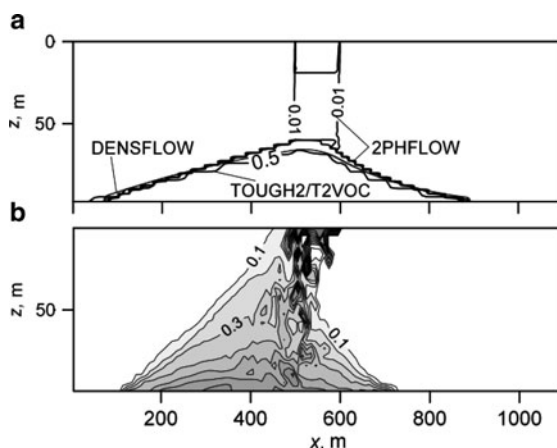


Fig. 14.11 The influence of model domain discretization on brine distribution under a surface reservoir (transport process simulation using TOUGH2/EOS7). $t = 15,000$ d. The horizontal and vertical size of model grid-blocks: (a) 10×5 m; (b) 2.5×2.5 m; (c) 2.5×0.5 m; (d) 2.5×0.25 m

A useful remark can be made in connection with the obtained results. Paradoxically, the algorithms of programs that suppress oscillations in numerical solutions proved to be less suitable for modeling migration processes in which fingering is an important component. However, program codes based on the methods of characteristics or Random Walk and admitting weak oscillations in numerical calculations are more suitable for describing the conditions of this type. Oscillations are a factor that “launches” the “channeling” transport mechanism; in a sense, they simulate the manifestation of microheterogeneities in the medium disturbing the *stability* of the originally horizontal freshwater and saltwater interface and hence to a jet-like subvertical motion of the dense liquid through the porous medium occupied by freshwater. Thus, the use of MOC3DD program with relatively coarse grid in the model domain (110×20 grid-blocks, 10×5 m) allowed jet-type motion of liquid under the bed of the basin to be reproduced in the model (Fig. 14.10). To obtain such result with TOUGH2/EOS7 program required high-resolution discretization of modeling domain (440×400 grid-blocks, 2.5×0.25 m; Fig. 14.11).

14.2.2.3 Schincariol and Schwartz Test (Reproduction of a Physical Experiment)

Numerical codes TOUGH2/EOS7, GEON-3DM, TOUGH2/T2VOC, SEAWAT, and 2PHFLOW, which calculate liquid flow and solute transport in a saturated porous media, have been validated against a laboratory experiment involving the injection of saline water into a tank filled with dispersed material (Fig. 14.12).

The laboratory 2D experiment was carried out and described by Schincariol and Schwartz (1990) and Schincariol et al. (1997). A tank (106.8×71 cm) with artificial dispersed material was filled with freshwater with a density of 998.2 kg m^{-3} . The head differential between the left and right boundaries of the model was chosen to maintain a hydraulic gradient producing water flow with a specific discharge of 0.1 m day^{-1} . A sodium chloride solution with different mineralization (from 1 to 100 g L^{-1} that corresponds to the density range from 0.999 to 1.0681 g cm^{-3}) was fed into the tank through a small window (5 cm in height) on the left boundary. In particular, the authors of that study have shown that even an insignificant density gradient ($\Delta\rho = 3.7 \text{ kg m}^{-3}$, corresponding to water mineralization difference of about 5 g L^{-1}) has an appreciable effect on saltwater plume migration.

As can be seen in Fig. 14.12, an important feature is the tendency for gravitational instabilities to alter the plume shape. Instabilities are manifest by lobeshaped protuberances that formed along the bottom edge of the saltwater plume. The experimental parameters chosen for the model analysis of experimental results are given in Table 14.3. We simulated this experiment using several numerical models (Figs. 14.13–14.16); the model results are given for time of 1 day for different grids used in the model domain.

Multivariant calculations using TOUGH2/EOS7 package (model of miscible fluids) have shown that coarse grids yield physically unlikely results (Fig. 14.13a–c), since density convection cannot be correctly simulated when the model blocks are large, hence the role of density gradient in the subvertical displacement of saltwater plume in porous medium would be underestimated. When the size of the model

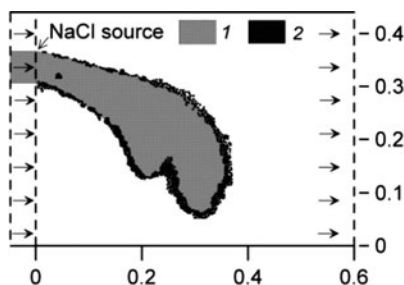


Fig. 14.12 A fragment of the physical model domain (Schincariol and Schwartz 1990). Grey color delineated by *dark edge* identifies the area occupied by saltwater (binary image was obtained for a 5 g/L NaCl source at $t = 1 \text{ d}$): (1) – 50–100% source concentration, (2) – 10–25% source concentration. Axes dimension is in m

Table 14.3 Parameters for the Schincariol and Schwartz test

Model characteristics	Values
Model length/height	0.5 m/0.5 m
Initial conditions	$\bar{C} = 0, \quad \rho = \rho_f = 998.36 \text{ kgm}^{-3}, \quad \mu = 0.001 \text{ kgm}^{-1} \text{ c}^{-1}$
Boundary conditions:	
Left side	$q = 0.1 \text{ md}^{-1}, \bar{C} = 0, \rho_f = 998.36 \text{ kgm}^{-3}, \mu = 0.001 \text{ kgm}^{-1} \text{ c}^{-1}$
Source	$q = 0.1 \text{ md}^{-1}, \bar{C} = 1, \rho_s = 1001.9 \text{ kgm}^{-3}, \mu = 0.001 \text{ kgm}^{-1} \text{ c}^{-1}$
Top and bottom	$q = 0$
Permeability, K	$5.71 \cdot 10^{-11} \text{ m}^2$
Porosity, ϕ	0.38

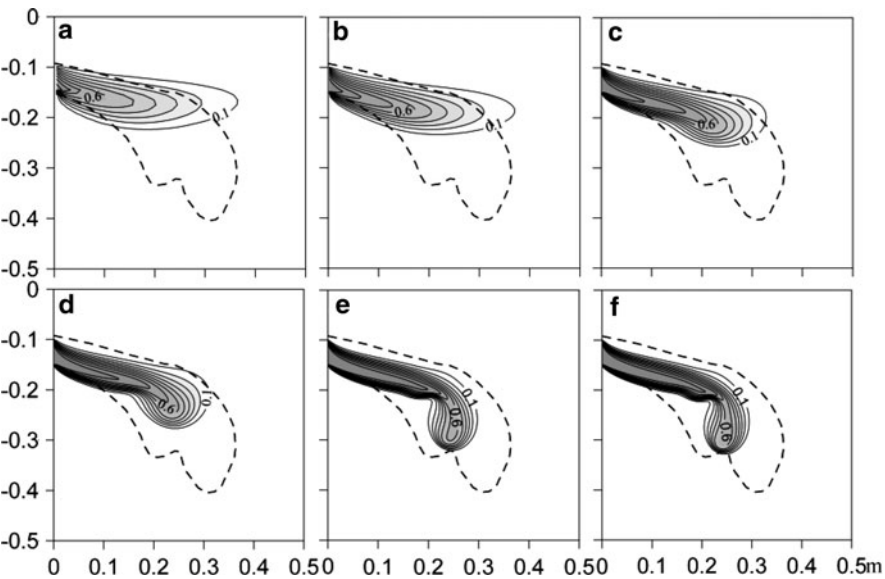


Fig. 14.13 The influence of model domain discretization on brine distribution (transport process simulation using TOUGH2/EOS7). The size of a model grid-block, mm: (a) 10, (b) 5, (c) 2.5, (d) 2, (e) 1.25, (f) 1. Here and in Figs. 14.14–14.16 dashed line identifies the area occupied by saltwater (10–25% source concentration)

block in the grid is comparable with the physical dispersivity ($\delta_L = 0.001 \text{ m}$, $\delta_T = 0.0002 \text{ m}$), the numerical result tends to become qualitative similar to the result obtained in the tank (Fig. 14.13d–f).

Note that the Schincariol and Schwartz test was reproduced by using a modulus of TOUGH2/EOS7 simulator, which neglects the physical dispersivity of the process. Therefore, even with a very fine partition of the model (250 000 model blocks, Fig. 14.13f), the brine sinks to the model bottom somewhat slower than in the laboratory experiment. It is worth noting that the fragmentation of the modeling domain in horizontal direction (and hence the longitudinal numerical dispersion) results in a greater effect of density gradient on the position of the leading front of brine than

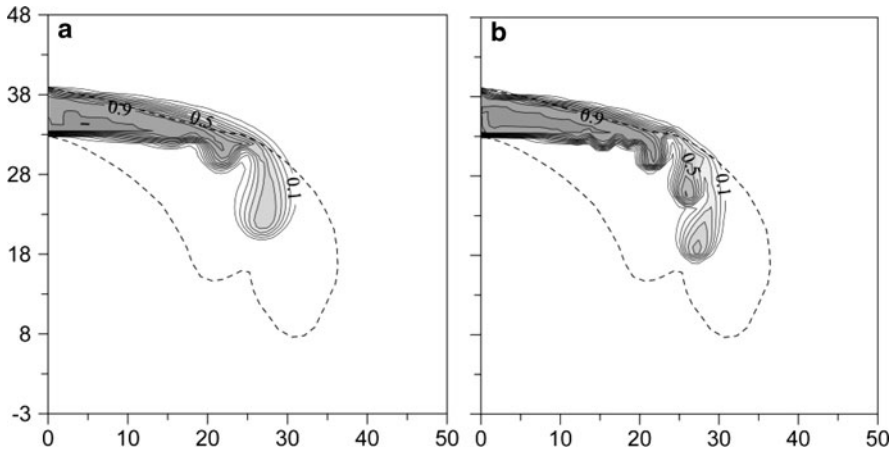


Fig. 14.14 Application of GEON-3DM for Schincariol and Schwartz test. Size of each model grid-block: (a) 2.5 mm; (b) 1.25 mm. Axes dimension is in cm

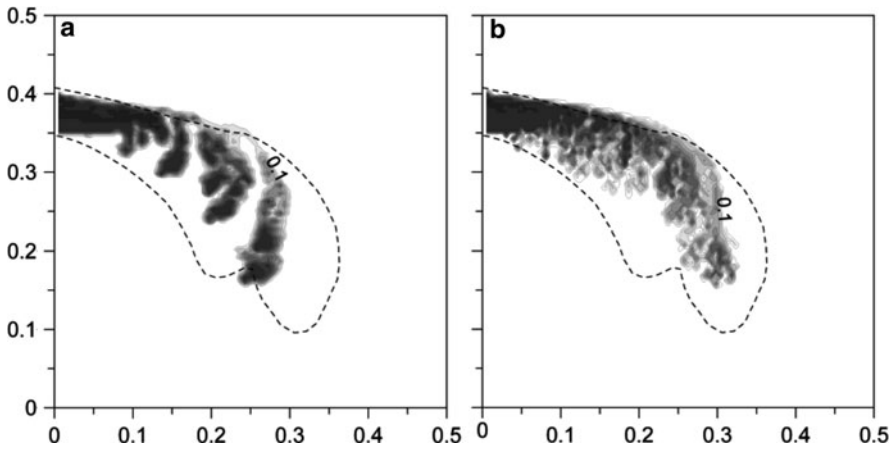


Fig. 14.15 Application of SEAWAT (MOC solver) numerical code for Schincariol and Schwartz (1990) test. The size of each model grid-block is: (a) 5 mm; (b) 1 mm. Axes dimension is in m

the vertical fragmentation. This fact has also been observed before in the analysis of solutions of other problems of saltwater intrusions (see, in particular, an example of a stratified aquifer described in Sect. 14.2.2.1).

A similar problem was solved using a GEON-3DM and SEAWAT numerical simulators (Figs. 14.14 and 14.15), which take into account the real (physical) dispersion of salts in groundwater flow. The obtained results appear quite impressive from the viewpoint of the manifestation of effects of gravitational instability of the saltwater–freshwater interface. Comparison of Fig. 14.13 shows that isolines of the concentration function $\bar{C}(x, z)$ obtained by the program TOUGH2 are smoother and do not reflect the process features reproduced by GEON-3DM and SEAWAT codes.

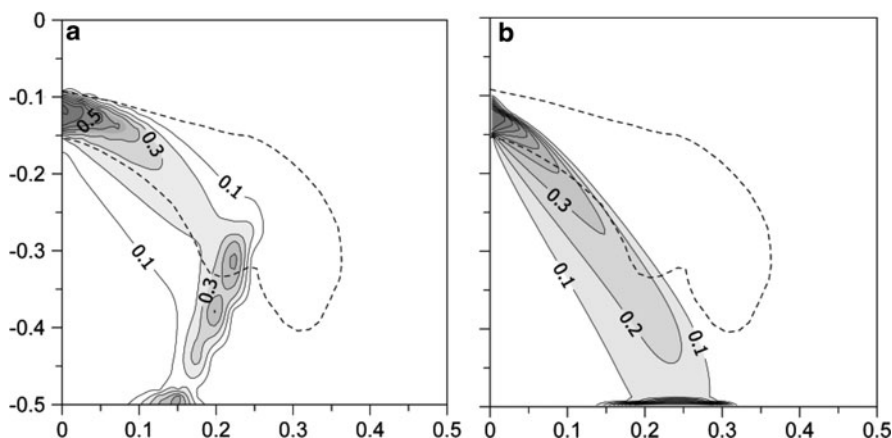


Fig. 14.16 Application of 2PHFLOW (a) and TOUGH2/T2VOC (b) numerical codes for Schincariol and Schwartz test. The size of each model grid-block is 5 mm. The intensity of grey color reflects the saturation of the aqueous phase with brine

Moreover, in the context of notes made above regarding the formation of saltwater intrusion under the basin bed (Sect. 14.2.2.2), it is clear that the use of models admitting oscillations of numerical solutions proves to be better for modeling the Schincariol and Schwartz test (Fig. 14.15).

The results of solution of the problem in the modeling framework for two-phase flow in porous media (2PHFLOW and TOUGH2/T2VOC codes) differ from both the model results described above and the physical experiment (Fig. 14.16). This is due to the fact that the brine density in two-phase models does not depend on brine concentration and its saturation in the porous medium, but is a constant value, equal to the initial brine density. As one may see, the two-phase flow assumption leads to an underestimate of the plume spread in horizontal direction and an overestimate in the vertical one. It is interesting to mention that enhanced spreading of solute perpendicular to the ambient water flow field in two-dimensional experimental set-up shall result in some kind of backwater effect. However in the two-phase flow concept the plume remains penetrable for the ambient freshwater flow.

14.2.3 Solute Concentration in a Pumping Well Affected by Saltwater–Freshwater Interface Upconing

As was formulated in Sect. 12.3, saltwater upconing may occur when a pumping well is installed in a freshwater reservoir underlain by layers containing saltwater. The list of analytical expressions for describing the changes in salt concentration in the pumping-out well caused by displacement of the interface between waters with different densities ($\Delta\rho > 0$), is quite limited (Kisel and Abramov 1978; Paster and Dagan 2008). The solution obtained by Kisel and Abramov (1978) in the form of

an integro-differential equation is very inconvenient to use in practical calculations. The solution given in the paper of [Paster and Dagan \(2008\)](#) refers to the steady-state case when a saltwater upcone is located below the water intake zone and describes salt input into a well from the domain of dispersion “erosion” of the contact between different-density liquids.

In this section we try to find more universal analytical relationships for approximating the numerical transient solutions of the saltwater upconing problem in a wide range of parameters, considering the situation when the yield of an incompletely penetrating well exceeds the critical value, Q^* (Sect. 12.3) and the hydrodynamic dispersion of the solute can be neglected. The solution for the case $\Delta\bar{\rho} = 0$, considered in Sect. 8.5.2, is used here as a limiting, reference solution; it is also of use in the substantiation of approximation formulas.

To study transient variations of salt concentration in the discharged water, $C(t)$, a simplified numerical model was developed on the base of TOUGH2/EOS7 code ([Pruess 1991a](#); [Pruess et al. 1999](#); see also Sect. 14.1). To check the reliability of numerical approach for simulating density-dependent transport, an alternative numerical model was designed using SUTRA code, v. 2.1 ([Voss and Provost 2002](#)). The models allowed one to check the validity of the analytical solutions and to obtain empirical equations for transient variations of salinization of a pumping well. The results of analytical and numerical experiments were then applied to the case of brine upconing at the Korshunovsky ore deposit site (Esatern Siberia, see Chap. 17).

14.2.3.1 Model Design and Modeling Scenarios

A two-dimensional (cylindrical) model (Fig. 14.17) was developed for simulating the advective solute transport in an aquifer with a sharp interface between freshwater and underlying saltwater of infinite thickness, $b \ll m$, where $b \equiv h_0$ is the thickness of the freshwater zone, m is the total thickness of the formation. In the present study, a reference numerical test-case (Table 14.4) and a set of supplementary tests (Table 14.5) were performed. In each test, only one parameter was modified compared to the reference variant: Q_w , ρ_s^0 , k_r , k_z , l , b (see Table 14.5a–f, respectively). Here Q_w is the volumetric well discharge rate [L^3/T]; ρ_s^0 is the saltwater density [ML^{-3}]; k_r and k_z are the hydraulic conductivities of the aquifer in lateral and vertical directions [LT^{-1}]; l is screen length, [L]; b is the thickness of the freshwater zone [L]. Table 14.6 summarizes the combinations of the input parameters. Thus, 27 model variants were analyzed to study the behavior of the concentration function.

Spatial discretization was kept unchanged for all the tests: the domain was divided into 90 layers and 30 radial blocks with a block size increasing logarithmically from the well to the external boundary. Figure 14.18 shows that further refinement of a model grid would not improve the accuracy of the analysis.

Numerical dispersion was negligible as expected from EOS7 numerical scheme and was proved by simulation tests for the major range of concentrations (Fig. 14.18). However, for $\bar{C} < 0.1$, numerical dispersion caused the divergence of simulation results from the analytical solution of Eq. 8.75 (where $h_0 \equiv b$ is the thickness of the freshwater zone).

Fig. 14.17 2D model domain: (a) presentation by uniform blocks (N_r and N_z are the numbers of blocks in r and z directions), and (b) actual discretization of the domain [$\Delta r(N_r = 1) = 0.1$ m, $\Delta r(N_r = 30) = 2990.9$ m; $\Delta z(N_z = 90) = 2$ m, $\Delta z(N_z = 1) = 73.4$ m]. The dash-and-dot line is the interface between the freshwater and saltwater

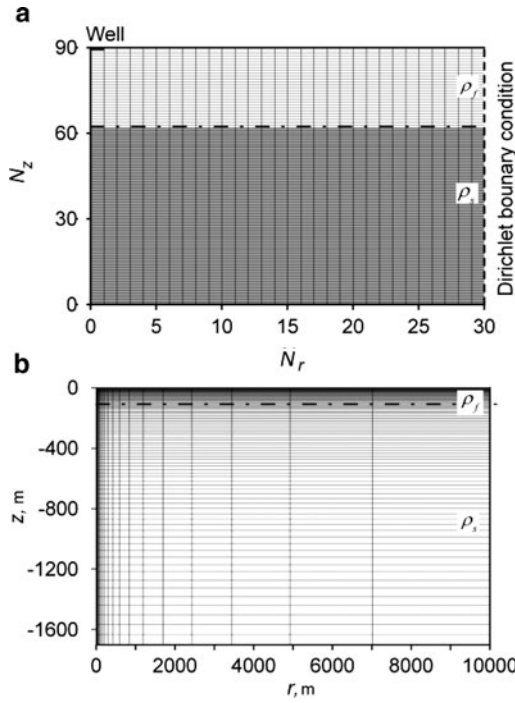


Table 14.4 Input parameters for the reference variant

Parameter	Value	Parameter	Value
$k_r = k_z$	0.5 m day^{-1}	Q_w	$1,000 \text{ m}^3 \text{ day}^{-1}$
ϕ	0.05	l	2.0 m
ρ_s^0	$1,070 \text{ kgm}^{-3}$	B	98.97 m
ρ_f^0	998.8 kgm^{-3}	m	1,700 m
$\Delta \bar{\rho}$	0.072244	R	10,000 m

All variants were required to satisfy the condition $Q_w/Q^* > 2$, where Q^* (critical pumping rate) is given by Eqs. 12.63. Below these limits, a strong role of dispersive transport was expected; the latter would not be possible to model correctly due to numerical dispersion. Additionally, for $Q_w/Q^* > 2$, the influence of fluid density on t_0 is still insignificant, which allows us to use Eq. 8.76a and to simplify, as it will be shown later, an analytical expression.

The pumping interval of a well was represented by several (i) model grid-blocks (in different model variants, i varied between 4 and 16); the resultant (total/average, $\bar{C}$) concentrations in discharged water were calculated as $\bar{C} = \sum \bar{C}_i Q_i / \sum Q_i$, where Q_i is the simulated water discharge from the i th model block of the well, $\bar{C}_i$ is the simulated dimensionless concentration in the i th block of the well.

Table 14.5 Model variants with different (a) well discharge rates, (b) densities of saltwater, (c) densities of saltwater for $k_r/k_z = 10$ ($k_r = 0.5 \text{ md}^{-1}$, $k_z = 0.05 \text{ md}^{-1}$), (d) densities of saltwater for $k_r/k_z = 0.1$ ($k_r = 0.05 \text{ md}^{-1}$, $k_z = 0.5 \text{ md}^{-1}$; $Q_w = 500 \text{ m}^3 \text{ d}^{-1}$), (e) screen lengths, and (f) thicknesses of a freshwater zone

Model variant	1	2	3	Reference	4	5	6
(a)							
Q_w , m ³ d ⁻¹	350	500	750	1,000	1,250	2,500	5,000
Q_w/Q^*	1.61	2.30	3.45	4.60	5.74	11.49	22.98
Model variant	7	8	9	Reference	10	11	11a ^a
(b)							
ρ_s , kg m ⁻³	1,000	1,020	1,050	1,070	1,100	1,150	1,250
$\Delta\bar{\rho}$	0.0021	0.0221	0.0522	0.0722	0.1023	0.1521	0.2525
Q_w/Q^*	160.6	14.99	6.36	4.60	3.25	2.18	6.57
Model variant	12	13	14	15	16		
(c)							
ρ_s , kg m ⁻³	1,020	1,050	1,070	1,100	1,150		
$\Delta\bar{\rho}$	0.0221	0.0522	0.0722	0.1023	0.1521		
Q_w/Q^*	12.5	5.31	3.83	2.71	1.82		
Model variant	17	18	19	20	21		
(d)							
ρ_s , kg m ⁻³	1,020	1,050	1,070	1,100	1,150		
$\Delta\bar{\rho}$	0.0221	0.0522	0.0722	0.1023	0.1521		
Q_w/Q^*	86.2	36.6	26.4	18.7	12.6		
Model variant	Reference	22	23	24	25		
(e)							
l , m	2	10.86	21.28	40.43	60.36		
β	0.0202	0.1097	0.215	0.4086	0.6099		
Q_w/Q^*	4.60	4.69	4.95	6.02	8.72		
Model variant	26	Reference	27				
(f)							
b , m	53.98	98.97	211.31 ^b				
β	0.0371	0.0202	0.0095				

^aHydraulic conductivity is 0.1 md^{-1} .

^bWell discharge: $5,000 \text{ m}^3 \text{ day}^{-1}$.

At the external boundary of the model domain ($r = R$), time-independent pressure was distributed along the z -axis according to the hydrostatic law (Dirichlet boundary condition, Fig. 14.17). The influence of the boundary ($R = 10,000 \text{ m}$, Table 14.4) on $\bar{C}(t)$ was significant after $\bar{t} = t/t_0 > 10^2\text{--}10^3$ (Fig. 14.19), which corresponded to tenths to hundreds of years for the reference variant. In case of a closer boundary, the breakthrough curve $\bar{C}(t)$ flattened earlier.

Table 14.6 Summary of the input parameters (variants' number)

		Discharge rate, $Q_w, \text{m}^3 \text{d}^{-1}$ ^a							Anisotropy, κ ^b		
$\rho_s, \text{kg/m}^3$	$\Delta\bar{p}$	350	500	750	1,000	1,250	2,500	5,000	0.1	1.0	10
998.8	0									+	
1,000	0.002									7	
1,020	0.022								12	8	17
1,050	0.052								13	9	18
1,070	0.072	1	2	3	Ref.	4	5	6	14	Ref.	19
1,100	0.102								15	10	20
1,150	0.152								16	11	21

		$\beta = l/b^a$				Thickness (m), m^d		
$\rho_s, \text{kg/m}^3$	$\Delta\bar{p}$	0.11	0.22	0.41	0.61	54 ($\beta = 0.04$)	99 ($\beta = 0.02$)	211 ($\beta = 0.01$)
998.8	0						+	
1,000	0.002						7	
1020	0.022						8	
1050	0.052						9	
1070	0.072	22	23	24	25	26	Ref.	276 ^e
1100	0.102						10	
1150	0.152						11	

^a $\kappa = 1$, $\beta = 0.02$, $b = 99 \text{ m}$.

^b $\beta = 0.02$, $m = 99 \text{ m}$, $Q_w = 1000 \text{ m}^3 \text{d}^{-1}$.

^c $\kappa = 1$, $m = 99 \text{ m}$, $Q_w = 1000 \text{ m}^3 \text{d}^{-1}$.

^d $\kappa = 1$, $Q_w = 1000 \text{ m}^3 \text{d}^{-1}$.

^e $Q_w = 2500 \text{ m}^3 \text{d}^{-1}$.

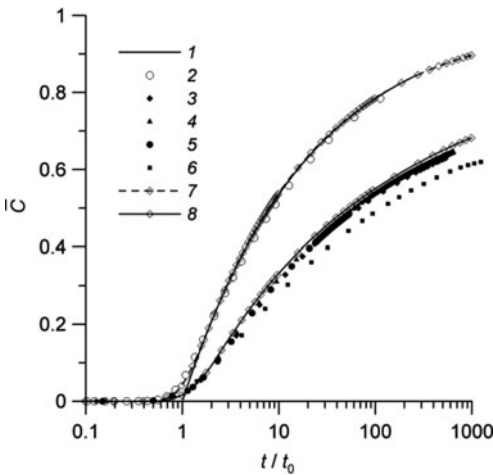
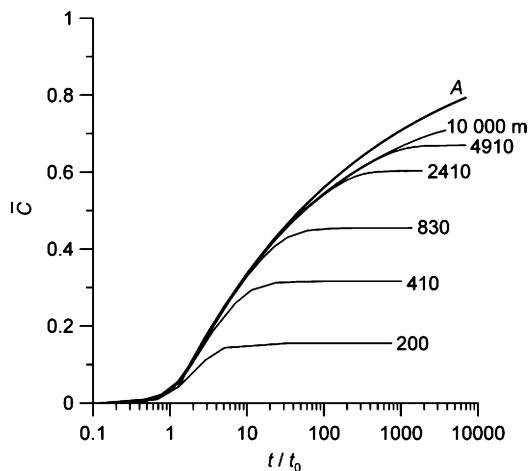


Fig. 14.18 Curves 1, 2: comparison of analytical solution (8.75) and numerical (grid 30×90) solution using TOUGH2 simulator for the variant with $\Delta\bar{p} = 0$. Curves 3–6: model variants (TOUGH2 results) with $\Delta\bar{p} > 0$ ($= 0.072244$) for a model domain discretized by different numbers of cells and layers: curve 3 – 30×90 (reference variant), curve 4 – 60×60 , curve 5 – 60×90 , curve 6 – 30×30 . Curve 7 and 8: SUTRA 2.1 results ($\Delta\bar{p} = 0$ and $\Delta\bar{p} = 0.072255$, respectively)

Fig. 14.19 Comparison between the analytical solution (curve A, Eq. 14.9) for an aquifer of infinite areal extent and those obtained from numerical simulations with different R (numbers at curves)



14.2.3.2 An Analytical Formula Approximating the Numerical Solution

The analytical function was obtained in the form of Eq. 8.75, which was transformed into:

$$\bar{C} = 1 - \left(\frac{f_0}{\beta} \right)^\lambda, \quad (14.7)$$

$$\lambda = f(\omega), \quad (14.7a)$$

where the exponent λ is a function of dimensionless well flow rate ω :

$$\omega = \frac{Q}{Q^{**}}, \quad Q^{**} = \frac{\pi}{3} k_r b^2 \Delta \bar{\rho}. \quad (14.8)$$

As was the case with the migration of constant-density solutions, the value of f_0 is defined by the transcendental formula (8.76).

At the first stage of model analysis, calculation variants (B, 1–21) were considered for an isotropic and anisotropic beds, water withdrawal from which was carried out through a well with a short screen ($\beta = 0.0202$). From the practical viewpoint, this is a point source, for which the expression (14.7) becomes

$$\bar{C} = 1 - \left(\frac{k^2}{\bar{t}} \right)^{\frac{\lambda}{3}} \quad (14.9)$$

($\kappa = \sqrt{k_r/k_z}$). In this case, the following functional relationship was chosen:

$$\lambda = 1 - \frac{1.7}{y} \left(1 + \frac{1}{4y^{(\ln y)^{-3/4} - 1}} \right), \quad (14.10)$$

where $y = e^{\sqrt{\omega}}$.

Thus, the exponent $\lambda(\omega)$ in formulas (14.7) and (14.9) controls the degree of convexity of function $\bar{C} = \bar{C}(\bar{t})$. The value $\lambda = 1$ is approached when $\omega \rightarrow \infty$, i.e., when the rate of water withdrawal Q_w is many times greater than the characteristic Q^{**} (14.8), depending on several parameters (b , k_r and $\Delta\bar{\rho}$). In this case, formula (14.9) transforms into solution (8.80), obtained for the case $\Delta\bar{\rho} = 0$.

Figures 14.20–14.23 show that Eq. 14.7 and its asymptotic representation (14.9) satisfactorily (with an error of less than 3–5% for the dimensionless concentration range greater than 0.1) approximate the results of numerical modeling for a wide range of input parameters (Table 14.6). A certain disagreement of numerical and analytical solutions occurs for long simulation times as a result of the influence of the external boundary (Fig. 14.19). For $\beta > 0.5$, the deviation of the numerical results from the approximate analytical solution dramatically increases (up to 15% for $\beta = 0.61$ – model variant with $l = 60$ m in Fig. 14.23a).

Fig. 14.20 Comparison between approximate analytical, Eq. 14.9 (curves), and numerical (circles and rhombuses) solutions for different well discharge rates (values in the legend, $\text{m}^3 \text{d}^{-1}$)

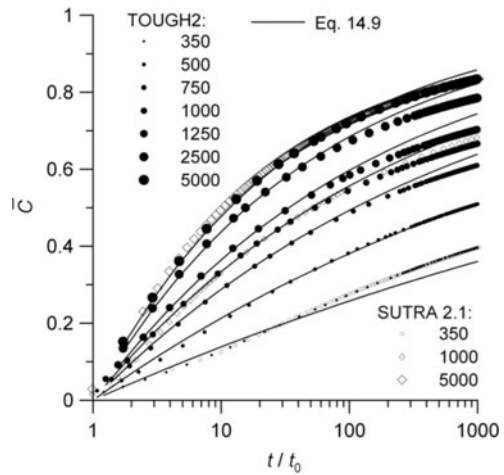
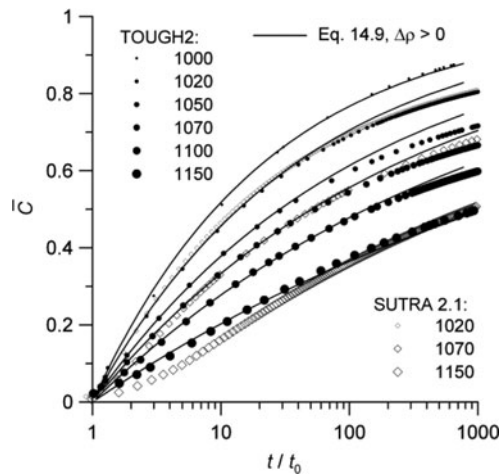


Fig. 14.21 Comparison between approximate analytical, Eq. 14.9, $\Delta\bar{\rho} > 0$ (curves), and numerical (circles and rhombuses) solutions for different density gradients (values in the legend, kgm^{-3})



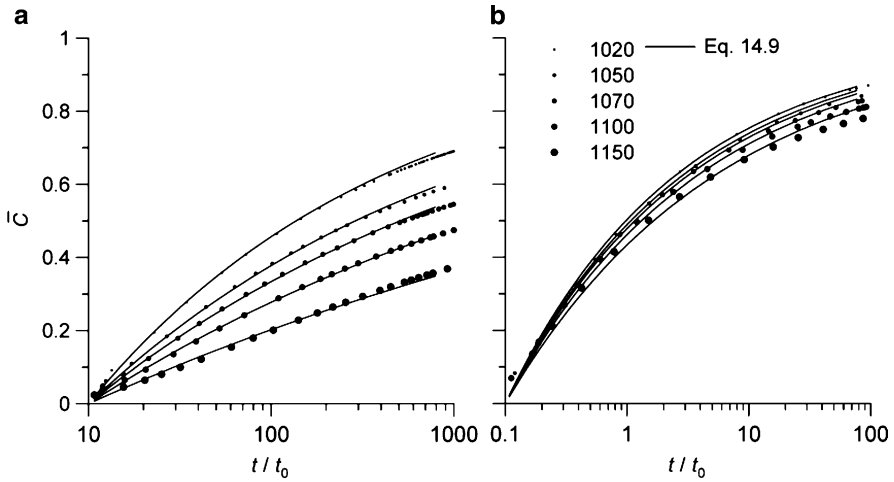


Fig. 14.22 Comparison between numerical (*circles*) and approximate analytical, Eq. 14.9 (*curves*), solutions of the saltwater upconing in anisotropy aquifer problem. (a) Model variants 12–16; (b) model variants 17–21. Numbers in the legends correspond to different saltwater densities (values in the legends, kgm^{-3})

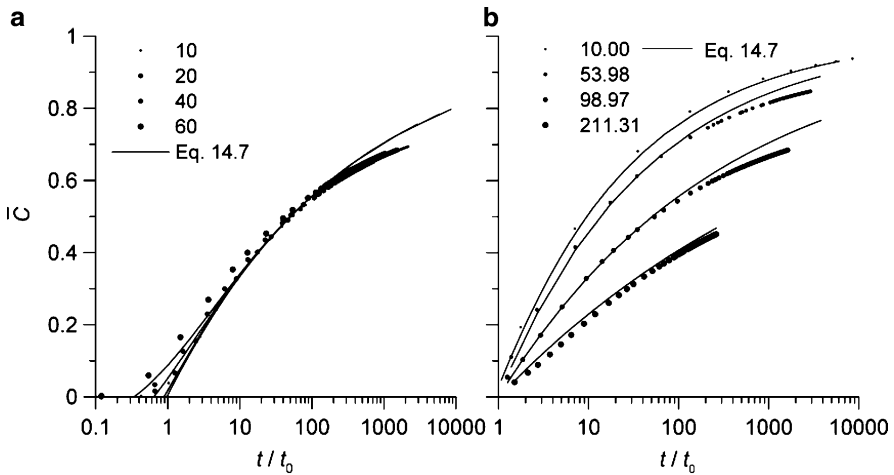


Fig. 14.23 Comparison between full analytical solution, Eq. 14.7 (*curves*), and numerical (*circles*) solutions: (a) for different screen lengths (values in the legend, m); (b) for different thicknesses of the freshwater zone (values in the legend, m)

The numerical modeling showed that density variations (for $\Delta\bar{\rho} \leq 0.25$) do not influence t_0 ; thus, once obtained for the case of $\Delta\bar{\rho} = 0$, it can be extrapolated for the density-dependent transport. However, the transient function $\bar{C}(t)$ is highly dependent on saltwater density. Even for comparatively low density contrast between

freshwater and saltwater under certain hydrodynamic conditions (controlled by a critical pumping rate), errors due to the neglect of density gradient can be quite large (for example, 18% for $\Delta\bar{\rho} = 0.022$, $M \approx 30 \text{ gl}^{-1}$, seawater, see variant 8).

The further analysis showed that the general solution (14.7) is also valid only when the length of well screen does not exceed half the thickness of freshwater zone, $\beta \leq 0.5$ (Fig. 14.23a). Additional calculations carried out for different b and given in Fig. 14.23b, confirmed the applicability of approximations (14.7) and (14.10).

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Part VI

Case Histories of Subsurface Contamination by Industrial and Environmental Brines: Field Data Analysis and Modeling of Migration Processes

This part of the work demonstrates the potential for using numerical groundwater flow and transport models in environmental risk assessment of subsurface contamination by dense or light miscible liquid waste. We apply modeling technique to the analysis of cases that are common in hydrogeological practice and connected with:

- (1) leakage of hazardous dense wastes from a surface reservoir to the near-surface environment,
- (2) seawater intrusion into coastal aquifers,
- (3) uncontrolled discharge of a deep brine into mine drainage systems,
- (4) disposal of industrial waste in a deep geological formation using injection well clusters.

The designing of numerical models is accompanied by analysis of a variety of real field and experimental data drawn from many different field sites that can be of some interest for bridging the gaps still existing in our knowledge of contaminant hydrogeology.

Chapter 15

Radioactive Brine Migration at the Lake Karachai Site (South Urals, Russian Federation)

The Lake Karachai site plays a unique role in the advancement of knowledge of the subsurface behavior and fate of many hazardous radionuclides. It is located within one of the South Ural provinces in Russian Federation (Drozhko and Glagolenko 1997; Drozhko et al. 1997a, b, c; Petrov et al. 1994; Solodov et al. 1994, 2005). The site is connected with *Mayak* Amalgamated Industry (MAI), a plant, producing radioactive materials for military and civil needs.

Within the framework presented here the influence of different processes and interactions on the transport of radionuclides will be identified and analyzed. This will help to improve our understanding of subsurface radionuclide transport at the Lake Karachai site and to develop a proper methodology to be applied to this reservoir. This chapter focuses on different problems regarding both hydrodynamic and hydrogeochemical aspects of the contaminant transport in order to provide a general, although not conclusive, description and investigation of the problem under study.

15.1 Introduction Remarks

There are several surface radioactive waste (RW) reservoirs between two rivers, which have been used over 60 years for storage of low-level and intermediate-level RW. The largest of them is the reservoir known as Lake Karachai, which contains the total of $1.2 \cdot 10^8$ Ci. The leakage from the reservoir has resulted in a contamination plume traveling through the aquifer composed of fractured metavolcanic rocks (Figs. 15.1 and 15.2; see also Figs. 15.4 and 15.5). This site probably contains more radioactive contamination than any site in the world.

The high density of the RW and aquifer heterogeneity along with the absence of a well-developed aquitard have caused a complex three-dimensional spreading of the plume. As long as the volume of the plume increases, it tends to move toward the zones of groundwater discharge threatening surface water and groundwater wellfields.

Subsurface radionuclide transport at the Lake Karachai site is accompanied by a range of physical and chemical processes and interactions including: advection,

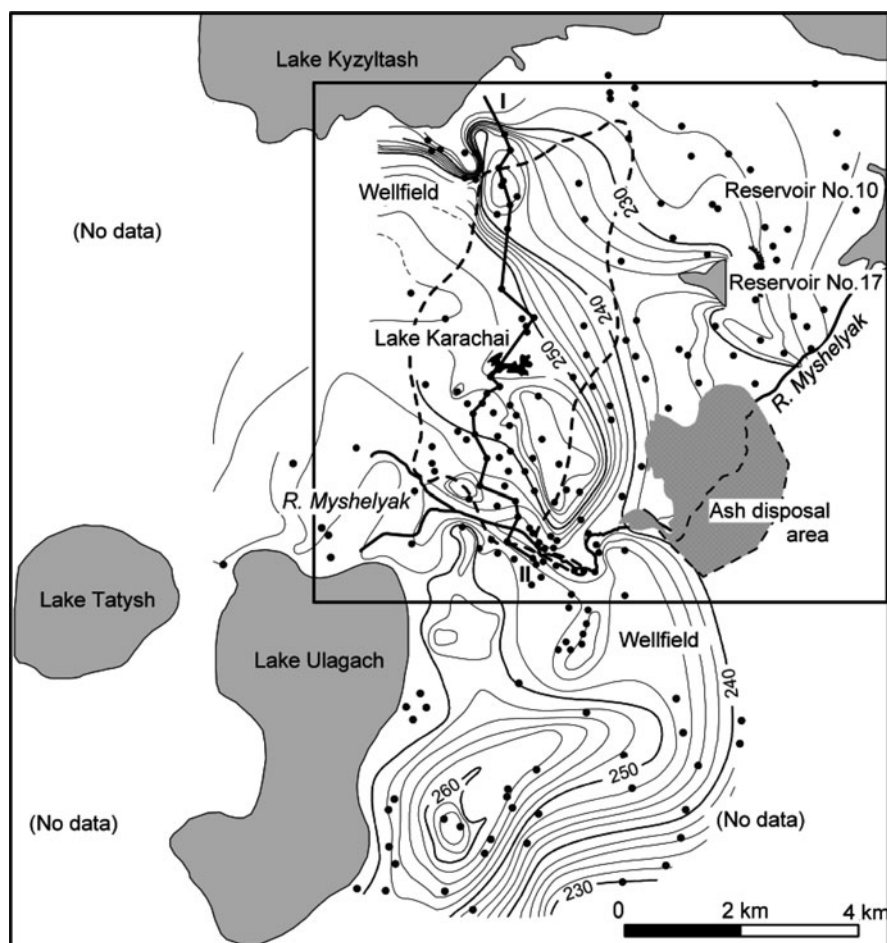


Fig. 15.1 Lake Karachai site map (regional model) and area selected for 3D applications (“window” model). Elevations expressed in meters above sea level (m, August, 1994). Small black dots are well locations. The dashes outline the nitrate pollution zone (45 mg/l, 1994). I–II is the section line (Fig. 15.2)

mechanical dispersion, chemical diffusion, radioactive decay, chemical reactions, and adsorption. Depending on the prevailing process or interaction, whose extent is a function of local geochemical conditions, the mass transport potential of the contaminant may be either enhanced or diminished.

Since November 1951, Lake Karachai (a former drainless high-moor bog) has been a discharge site of liquid industrial wastes (classified as medium-radioactive) high in nitrate salts (Fig. 15.1). Its water surface area varied in different years from 36 to 52 ha at a depth of 2–3 m. According to different estimates, from four to

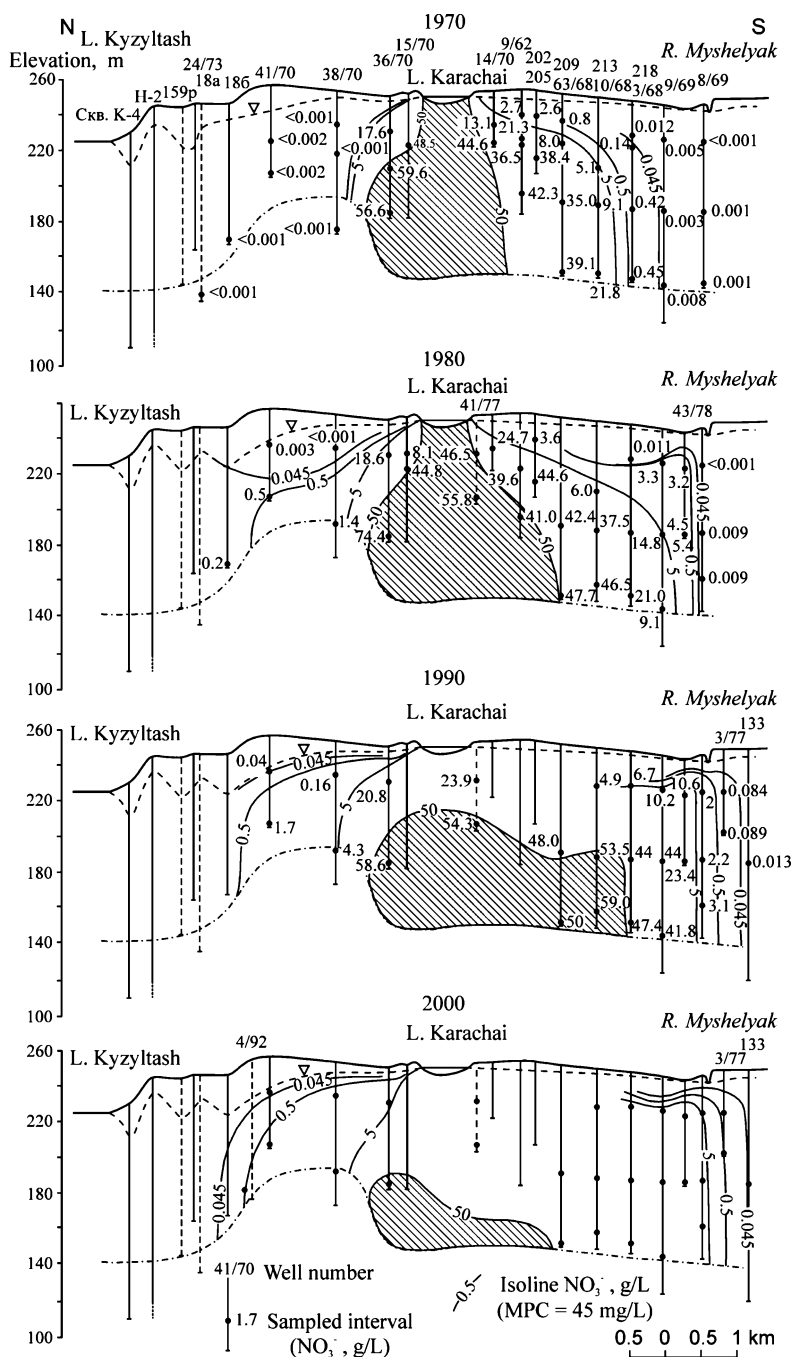


Fig. 15.2 Dynamics of groundwater contamination by nitrate brine, 1970–2000 (Samsonova and Drozhko 1996, with additions; Drozhko et al. 2007)

five million m^3 of liquid RW with a total activity of about $550 \cdot 10^6$ Ci has been discharged into Lake Karachai by 2004 (Ivanov 2004). The total activity of solutions that have reached groundwater is estimated at about 600,000 Ci. Rehabilitation works were launched in 1986, including the filling of the lake by hollow cement blocks meant to absorb radioactive wastes and reduce the hazard of wind spreading of radioactive dust in the period of lake drying (as may be the case after the anticipated cessation of waste discharge into the lake). Radioactive solutions are concentrated in the upper zone of weathering-crust rocks, represented mostly by lavas and tuff lavas of andesite–basalt porphyrites of Middle Silurian and Lower Devonian ($S_2 - D_1$) (Omelianenko et al. 1994; Solodov et al. 2005). These rocks belong to low or moderately alkaline varieties of base rocks.

In this chapter, we explore a possibility to study the radioactive brine migration utilizing different modeling concepts and numerical simulators. Both sharp-interface and fully miscible models are considered. Field and laboratory experimental data are used for computer code improvement.

15.2 Hydrogeological Setting and General Description of the Migration Process

The Lake Karachai site lies above an unconfined volcanic-rock reservoir, located within a water-divide domain in the Techa and Zyuzelga rivers' interfluvium. The groundwater potentiometric surface (Fig. 15.1) lies at a depth of 0.1–20 m (5–7 m on average). Under natural conditions, the aquifer is recharged primarily by precipitation. The groundwater recharge varies seasonally, with the bulk of the recharge falling within the period April–May. The average annual recharge rate is between 10 and 25% of the annual precipitation. The groundwater discharge area is associated with the river-plains and lakes, in particular, the Mishelyak River is a not fully penetrating drainage contour intercepting part of regional flow (Fig. 15.1). Water flow rates averaged over low-water periods vary within $0.15\text{--}0.3 \text{ m}^3/\text{c}$, while those for flood periods vary from 0.8 to $1.8 \text{ m}^3/\text{c}$. The mean annual runoff of the Mishelyak River in period 2000–2004 varied from about $13 \cdot 10^6\text{--}8 \cdot 10^6 \text{ m}^3$. Small natural water bodies are also natural drains.

The flow paths of subsurface natural and technogenic waters are associated with fissures of exogenous and tectonic origin. Analysis of the summary column for the weathering profile of andesite–basalt porphyrites, widely occurring in the Lake Karachai area, allows three zones of supergenically altered rocks to be identified: the zone of clayey alterations (with a thickness of up to 30 m), the zone of initial clayey alterations (up to 50 m), and disintegration zone (up to 80–90 m). Clearly, the presence of these zones largely determines the permeability profile for the groundwater flow. Tectonic fissures (linear zones of tectonites in the fault domain) form predominant groundwater flow paths (Solodov et al. 2005). In particular, Mishelyakskaya

fault zone (with a thickness of tens–hundreds meters) with NW–SE strike can be traced by topographic lows between Lake Karachai and the Mishelyak River (Ivanov 2004; Solodov et al. 2005).

According to the data obtained by means of different types of field techniques (pumping tests, slug tests, and geophysical logging of boreholes aimed at investigating the fractured massif structure as well as obtaining core-samples), the water-bearing rocks are highly heterogeneous. The transmissivity was shown to vary from 1 to 800 m²/day (according to the results of more than 300 pumping tests, Pozdniakov 1996), the most widespread rock blocks have transmissivity ranging from 20 to 500 m²/day. The logarithmic transmissivity variance is rather high. Ordinary kriging (Deutsch and Journel 1992) of the logarithm of transmissivity was used for creating the map of expected transmissivity values (Pozdniakov 1996; Drozhko et al. 1997c; Rumynin et al. 1998). As a result of kriging interpolation, the conditional expected mean $m_{\ln T}$ of the logarithm of transmissivity in the grid nodes was defined. The resulting transmissivity map was represented by Rumynin et al. (1998). As one could expect, the areal distribution of the parameter proves to be complex and almost unpredictable. It represents a combination of large blocks of low transmissivity and narrow elongated zones of high transmissivity.

The hydraulic conductivity distribution is nonuniform in the vertical cross-section, and one can discern 3–4 zones. These are (from top to bottom):

- a low-permeability zone-1 ($k = 0.1\text{--}0.5$ m/day),
- a relatively high-permeability zone-2 ($k = 0.5\text{--}5.0$ m/day),
- a low-permeability zone-3 ($k < 0.1$ m/day).

The vertical position of the underlying bedrock is uncertain due to the monotonous decrease in permeability and fracturing. The choice of assigning the elevation of the bottom boundary of the fractured-permeability zone is a matter of convention. Thus, it was assumed that conditional bedrock lies at a depth of about 100 m below land surface (Petrov et al. 1994). The intensity and character of fissuring in the rock formation can be understood from the curves in Fig. 15.3 constructed by the results of field studies (Drozhko et al. 1997b), including downhole telephotometry and description of the core from wells located north (Northern domain, 12 wells) and south (Southern domain, 17 wells) of Lake Karachai. It can be clearly seen that the *fracture porosity* exponentially declines with depth from 1.5% to 2% in the top of the cross-section to 0.1–0.4% at depths over 50 m. The mean distance between fractures ranges from 0.1 to 0.05 m (in the top of the cross section) to 1 to 5 m (near the bottom). The *porosity of the rock matrix* is within the range 0.2–1.0%.

Molecular diffusion controls solute exchange between fractures and porous matrix. Its intensity can be characterized by the coefficient D_e , which is of the order of 10^{-8} m²/day (Rumynin et al. 1998).

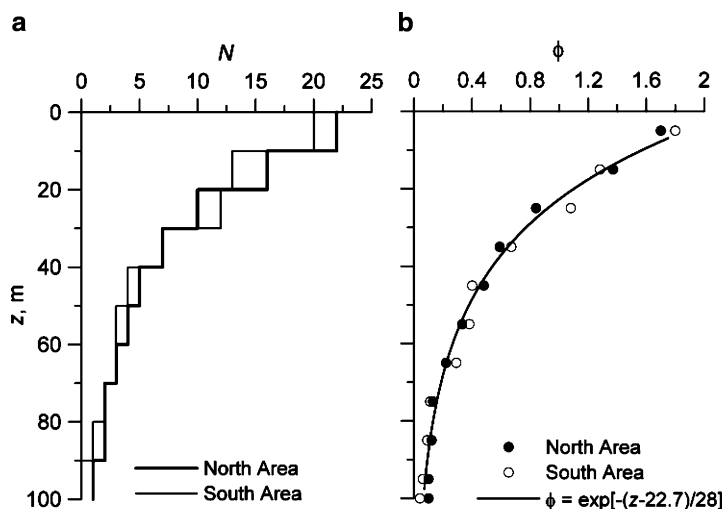


Fig. 15.3 Plots of distributions of (a) fracture density and (b) fracture porosity over depth. N is the number of fractures per 1 m of core sample, ϕ is fracture porosity, %

15.3 Groundwater Contamination Plume

15.3.1 A Structure of Groundwater Flow at the Site

Observations of the plume (see Figs. 15.1, 15.2, 15.4, and 15.5), including a system of hydrogeological and geophysical studies and mathematical modeling of migration process, allow us to conclude that the leading front of salt solutions have reached the contours of natural (the Mishelyak River valley) and technogenic (water intakes for service needs, located near the Techa system) groundwater drainage that are closest to Lake Karachai (Solodov et al. 1994; Drozhko et al. 1997a, 1997b). The sorption effects, accompanying solute migration, result in radioactive pollution front moving slower than the groundwater flow. This, however, can be only temporary retention, which does not reduce the hazard of radioactive pollution of surface water in the nearest future. Of greatest hazard is the southward flow of substandard water toward the Mishelyak River valley, creating a pollution hazard to clear river water and floodplain deposits. Nowadays, the southern boundary of the pollution plume is dangerously near the water intake wells of Novogornyi Settlement on the right bank of the Mishelyak River.

The rate of water losses from Lake Karachai through seepage has increased from several tens of cubic meters per day in the first years of its use to 200–500 m³/day in the late 1960s–early 1970s. After that, the leakage started decreasing because of the general reduction of discharge volumes and the filling of the lake by solid materials: the seepage losses were 30–40 m³/day in the mid-1990s. According to balance estimates, the total leakage volume over the period from 1951 to 1996 was about $3.4 \cdot 10^6$ m³.

Because of some features of the process used in the 1950s–1960s, the wastes discharged into Lake Karachai contained large amounts of salts. As a result, the total concentration of salts (C_s) in lake water has reached 100–145 g/L by the early 1970s, including 69–78 g/L of nitrate ions (the dominating component). Under such conditions, the solution density was 1.06–1.095 g/cm³. After a change in the nuclear fuel processing technology in 1971, the salt content of liquid wastes discharged into the lake started decreasing. In the late 1990s, the concentration of inorganic salts in the lake did not exceed 20 g/L, and solution density was 1.01–1.02 g/cm³. Organic compounds dissolved in water are acetate (CH_3COO), 0.6–20 g/L, and oxalate ($\text{H}_2\text{C}_2\text{O}_4$), 0.9–14 g/L. The solutions accumulating in the lake are alkaline (pH 7.9–9.3).

The migration of solutions is accompanied by processes such as density-induced (i.e., caused by the density difference between industrial and natural waters) and natural (under the effect of gradients of natural flow field—in the periphery of the plume) convection in fractures, longitudinal and transverse hydrodynamic dispersion, and molecular diffusion within blocks (rock-matrix).

The plume boundaries mapped using nitrate (a conservative component) and radionuclide concentrations are moving largely southwards and northwards from the reservoir (Fig. 15.1) at a velocity of 70 to 80 m/year (Drozhko and Glagolenko 1997). The velocities of the radionuclides movement are noticeably lower. Due to the increased density, the plume first sinks to the aquifer bottom, and then migrates laterally, commonly, between depths of 40 and 100 m. An intrusion of high-density solution can be identified in the pollution plume (Fig. 15.2). It is situated symmetrically relative the basin: its southern boundary in the middle plane of the aquifer is shifted 1.5–2.0 km toward the Mishelyak River valley, while its northern boundary lies near the shoreline of the basin. In the south, the advancing front of the NO_3 plume has reached the Myshelyak River at depth of over 60 m.

The predominant direction of brine migration, as well as the plume shape are not consistent with the monitored hydrodynamic data: the maximum values of potentiometric gradients are recorded in the northeast direction (Fig. 15.1), while the actual plume moves southwards. This unexpected behavior is supported by hydrodynamic and groundwater quality monitoring data. This leads us to the development of a new conceptual approach for trying, on the one hand, to explain this apparent conflict with the expected results, and, on the other hand, to enable us to make predictions on the migration of the brine and radionuclides under this unique hydrogeological scenario.

15.3.2 The Distribution of the Radionuclides and Principal Ions Within Contamination Plume

In addition to nitrate ion, the main indicator components that were in use until the mid-1990s for assessing the rates of groundwater pollution processes (Fig. 15.4a) were tritium, strontium-90, ruthenium-106, cobalt-60 (Fig. 15.4b), and acetate ion.

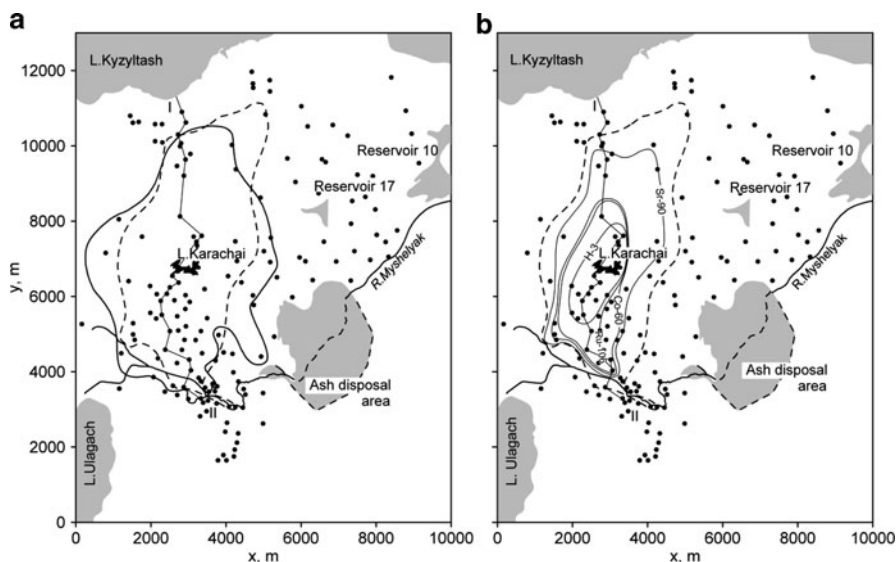


Fig. 15.4 The character of groundwater pollution near Lake Karachai. **(a)** The dynamics of groundwater nitrate pollution development (*dashes* are for concentration contour $\text{NO}_3^- = 45 \text{ mg/L}$ as of 1994, the *full line* is the same for 2005); **(b)** the plume of groundwater pollution by radionuclides (concentration contours correspond to MPC established by Safety Standards UV/NRB-99). Dots are observation wells, I–II is the section line (see Fig. 15.2)

According to data of well sampling in 1993–1994, the concentrations of radionuclides, such as Sr-90, Cs-137, Co-60, and Ru-106 near the basin were many times (three to five orders of magnitude) greater than the admissible levels (Table 15.1). The same pollution level in terms of Sr-90 and Cs-137 in the areas adjacent to the basin has persisted until now. An additional series of monitoring-type studies were carried out in 2001–2003 to examine the migration process in more detail, identify additional “markers” of groundwater radioactive pollution, such as uranium and transuranium (actinides) elements (Fig. 15.5). In 2007, data on the presence of significant concentrations of technetium (Tc-99) in groundwater in the area near the industrial water bodies were obtained for the first time (Fig. 15.5).

The radiochemical studies were primarily aimed at studying the distribution of uranium and actinides in different media, including the liquid phase of technogenic water accumulating in the basin, bottom sediments in its base, groundwater, and the groundwater-bearing rocks.

The results of this comprehensive study and their comparison with the data of earlier sampling have shown (Drozhko et al. 2007) that the volumetric activity of the total of alpha-emitting nuclides in lake water was in all times about four orders of magnitude below the specific beta-activity. U concentration varied between 7 and 215 mg/L (the volumetric alpha activity of $2.7 \cdot 10^3$ – $6.3 \cdot 10^5 \text{ Bq/L}$). Analysis of water samples taken in 2002 (Table 15.2) made it possible to establish that americium (Am-241) and curium (Cm-244) dominated among actinides, and the major

Table 15.1 Radionuclide concentrations (Bq/L) in polluted groundwater of the southern branch of the flow (Fig. 15.1) according to data of sampling in 1994–1995 (Novikov et al. 1998)

Characteristics	R-9 ^a	Well number						
		41/77	63/68	64/68	65/68	3/68	8/69	176
Distance, m	0	50	1,100	1,460	1,770	1,900	2,400	2,500
Depth, m	0	45	20	100	100	100	80	27
Cs-137	$4 \cdot 10^6$	$14 \cdot 10^4$	490	290	80	ND ^b	ND ^b	ND ^b
Sr-90	$9.5 \cdot 10^6$	$78 \cdot 10^4$	$31 \cdot 10^4$	$18 \cdot 10^4$	$57 \cdot 10^4$	$1 \cdot 10^5$	90	1,400
Co-60	ND	$15 \cdot 10^3$	3,300	1,300	890	5,300	14	118

^a Lake Karachai

^b No data available

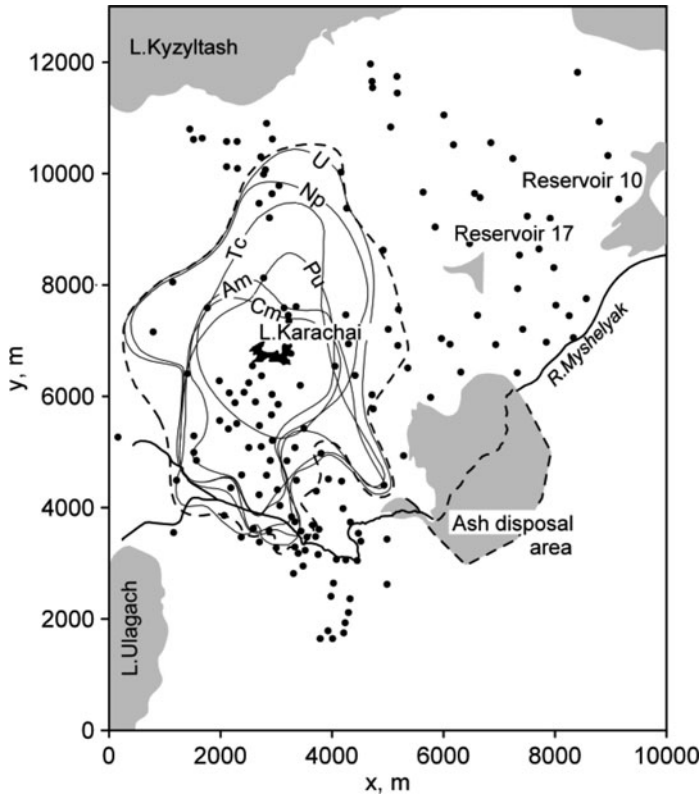


Fig. 15.5 Scheme of occurrence of uranium, actinides, and technetium (in the maximum-concentration plane) in groundwater by the results of sampling in 2001–2007 (Ivanov 2004; Ivanov et al. 2005). The plumes are outlined by concentrations corresponding to the values of MPC (Safety Standards UV/NRB-99): U = 75 mg/L, Np-237 = 1.3, Pu-239,240 = 0.56, Am-241 = 0.69, Cm-244 = 1.2, Tc-99 = 220 Bq/L

portion of actinides (60–90%) in liquid phase is associated with suspended particles; the contribution of adsorption of Sr-90 and Cs-137 on suspended particles

Table 15.2 The distribution of uranium, actinides, and technetium (Ivanov et al. 2005)

Environment, characteristics	$^{235+238}\text{U}$	$^{239+240}\text{Pu}$	^{241}Am	^{244}Cm	^{237}Np	^{99}Tc
MPC ^a	2.9–3.1	0.56	0.69	1.2	1.3	220
Waste ^b	$1.2 \cdot 10^4$	$9.0 \cdot 10^4$	$8.5 \cdot 10^{5e}$	$6.2 \cdot 10^5$	$3.3 \cdot 10^{3f}$	$2.1 \cdot 10^4$
Bottom sediments ^c	$6.3 \cdot 10^5$	$1.2 \cdot 10^9$	$1.2 \cdot 10^{10e}$	$2.3 \cdot 10^9$	$2.0 \cdot 10^{7f}$	
Groundwater ^d	$2.3 \cdot 10^3$	2.1	6.4	14.0	18.2	$\sim 1 \cdot 10^4$

^aMaximum permissible concentration (Safety standards UV/NRB-99)^bVolumetric activity (VA), Bq/L^cSpecific activity (SA), Bq/(kg dry sediment)^dVolumetric activity (VA), Bq/L^e $\downarrow^{238}\text{Pu}$ ^f $\downarrow^{234}\text{U}$

never exceeded 3–5%. The total “reserve” of beta-active nuclides (Sr-90, Cs-137) in the water, silts, and underlying loams is about 22 million Ci, that for alpha-emitters (Am-241; Pu-238, 239, 240; Cm-244; isotopes of U) is about 0.7 million Ci (Drozhko et al. 2007). Laboratory experiments have shown a very low degree of radionuclide desorption from technogenic silts. Notwithstanding this fact, in the case of many-year water flow through silts, a considerable portion of these radionuclides reaches the aquifer.

In the total radiation balance, 90–95% of the activity of beta-emitting radionuclides and more than 99% of the activity of alpha-emitting radionuclides are deposited in bottom sediments, mostly in the top 10–70-cm layer (Drozhko et al. 2007). Uranium is distributed in nearly equal parts between water and bottom sediments. The volumetric alpha-activity of uranium in both water in the basin and bottom sediments is 3–5 orders less than that of actinides. Again, the volumetric concentration of actinides in water is about four orders less than the specific activity of actinides in bottom sediments (Ivanov 2004; Ivanov et al. 2005).

A higher migration capacity is typical of Tc-99, which occurs in groundwater in a mobile anionic form TcO_4^- . The plume of Tc-99 pollution around the basin within the contour of maximal permissible concentration (MPC) is about 12 km² in area (Fig. 15.5).

Overall, analysis of the obtained data (Table 15.2, Fig. 15.5) leads us to the following conclusions.

- (1) The bottom sediments in the basin serve as a powerful sorption barrier for actinides on their path to the aquifer.
- (2) However, uranium isotopes are relatively weakly retained by these deposits.
- (3) The result is that uranium enters groundwater in concentrations practically equal to their initial level (tens of milligrams per liter), thus determining (by 90% and more) the level of their alpha-activity.
- (4) Technogenic uranium forms a very contrast plume in groundwater, where its maximal concentrations are several hundreds of times greater than the MPC value according to Safety Standards UV/NRB-99 (Table 15.2); these concentrations are associated with the undiluted-solution zones in the lower parts of cross sections and correspond to retrospective uranium concentrations in Lake

Karachai. Therefore, in the course of radiochemical monitoring, uranium can be regarded as a major indicator of groundwater radioactive pollution near Lake Karachai; the dominating ionic forms are $\text{UO}_2(\text{CO}_3)_2^{2-}$ (near the pollution source) and $\text{UO}_2(\text{CO}_3)_3^{4-}$ (at a distance from the pollution source) (Novikov et al. 2006).

- (5) The velocities of southward and northward migration of uranium isotopes, Np-237, Am-241, and Sr-90 obtained by averaging data of 40–45-year observations of groundwater pollution (these velocities can be evaluated by appropriate shifts of concentration contours at the level of MPC according to Safety Standards UV/NRB-99), approach the migration velocities of nitrate ion (50–60 m/year). The migration velocity of Cs-137, Cm-244, and Pu-239, 240 are somewhat less (30–50 m/year, on the average); with approaching the zone of potential discharge into river network, the displacement velocities of the concentration contours in these directions decrease and now they do not exceed 15–20 m/year.
- (6) The leading front of pollution by some radionuclides and nitrate ion has reached the Mishelyak River valley so that appreciable concentrations near MPC are recorded in wells located on the right bank of the river and spaced up to 300 m from the water edge (data as of 2004–2007). Moreover, water sampling from alluvial deposits of the Myshelyak river in the discharge zone of groundwater flow shows the presence of nitrates (between tens and few thousands of milligrams per liter) and Sr-90 (from a few to 10 Bq/L).
- (7) Additional thermodynamic calculations and laboratory studies (ultrafiltration through membrane filters) allowed us to establish that the higher mobility of uranium and neptunium in groundwater is due to the partial occurrence of these radionuclides as components of negatively charged or neutral anionic (weakly sorbed by rocks) complexes, while the higher mobility of plutonium and americium is additionally due to adsorption on high-mobility, colloidal (mostly inorganic) particles. The Pu recorded in groundwater was found to be 70–90 mol% sorbed onto colloids (Novikov et al. 2006; see also Sect. 27.3.1). An alternative explanation for Pu migration in groundwater is complexation with oxalate (Cantrell and Riley 2008). Uranium (as uranyl) and the majority of actinides (except for neptunium) form stable carbonate complexes under such conditions.
- (8) A close linear correlation was found to exist between the concentrations of uranium, actinides (Pu-239,240 and Np-237), and Tc-99 and the concentration of nitrate ion in groundwater; the existence of such correlation serves as an additional confirmation of the higher migration capacity of those radionuclides, whose behavior in groundwater, as well as the behavior of the inert nitrate ion, is largely controlled by advective–hydrodispersion mechanisms, rather than interphase interactions.

The main conclusion derived from the results cited here is that actinides and isotopes of U, when in high-mobility migration form, are an objective hazard to natural water quality in the region. The main barrier currently hampering radionuclide discharge into river water is represented by loamy deposits in the Mychelyak

River valley, because of their low permeability and high sorption capacity. Conversely, the adsorption of Tc-99 on this deposits features relatively low distribution coefficients ($<6 \text{ cm}^3/\text{g}$).

Direct radioisotope studies of core material taken during the drilling of wells no. 5/190 (400 m north of Lake Karachai), 1/99, 1/99A, and 2/99 (1–2 km south of Lake Karachai) confirm the possibility of sorption retention of radionuclides (Novikov et al. 1998; Ivanov 2004; Drozhko et al. 2007). Analysis of published data allows us to note that (a) radionuclides concentrate mostly on the surface of fractures covered by secondary minerals; (b) the penetration of radionuclides into the pore matrix (“near-fracture” fringe) can reach 5–7 mm; (c) by the degree of their activity in the solid phase, radionuclides form the series $\text{Sr-90} > \text{Cs-137} > \text{Ru-106}$ and $\text{U-238} + \text{U-234} > \text{Pu-239} + \text{Pu-240}$, with the specific activity of U in the secondary mineralization reaching 1500–2000 Bq/kg in some cases. Data on Sr-90 content of rock (the mean activity of radionuclide in the crashed mass of the core taken from different intervals in wells) and water were used to calculate the coefficients of sorption distribution K_d ; the results are (cm^3/g): 0.056 for the top, most permeable zone of the section; 0.006 for the middle zone; and 0.003 for the bottom (low-permeability) zone (Drozhko et al. 2007).

Overall, the migration of radioactive solutions in the area under study is accompanied by various hydrochemical intraphase and interphase interactions (Rumynin et al. 1998; Solodov et al. 2005; see also experimental material in Sect. 23.3). Along with the common and well-known processes, radiogenic metamorphization of technogenic waters takes place (Solodov et al. 2005). The authors of that work consider the effect of internal (dissolved radionuclides) and external (radionuclides adsorbed on fracture walls) sources of corpuscular α -, β -, and γ -radiation on the stability of acetate and oxalate in the solution. It is the destruction of these compounds under the effect of radiation that leads to the appearance in polluted waters of anomalous concentrations of carbon dioxide (CO_2). Moreover, the elemental hydrogen that forms during the destruction of acetate can reduce nitrate (NO_3^-) to nitrite (NO_2^-) and ammonium (NO_4^+), whose higher concentrations are also recorded in polluted waters (Fig. 15.6a), thus contributing to an increase in dissolved oxygen concentration (O_2).

This direction of the process leads to the formation of subacid (pH 5.6–5.9) carbon-dioxide nitrate sodium solutions that are highly corrosive with respect to rocks (Fig. 15.6b). The increase in the acidity of anthropogenic solutions during their movement along the bed is also accompanied by an increase in the oxidation potential to +510 mV against background conditions, compared to background values (in unpolluted areas) of (+50) – (+275) mV. This potential is presumably controlled by the system $\text{NO}_2^-/\text{NO}_3^-$ (Solodov et al. 2005). A cause of the high values of oxidation potential can also be water radiolysis.

The within-bed motion of high-mineralization solutions, experiencing radiogenic transformation in the fracture space, leads, in its turn, to leaching alkaline-earth elements, potassium, and stable strontium from rocks (Fig. 15.6c). The concentration of these elements in the leading zone of the “leaching wave” in polluted waters reaches anomalously high values (mg/L): up to 10,800 for Ca, 4,500 for Mg, 260

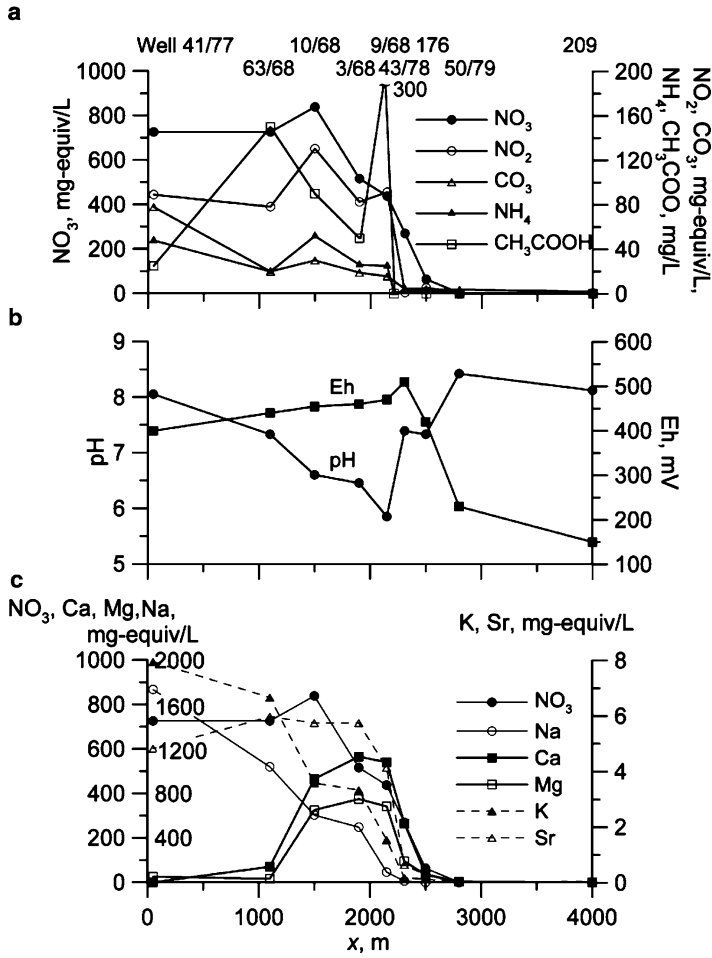


Fig. 15.6 Variations in the composition and hydrochemical characteristics of the groundwater contamination plume. (a) Nitrogen compounds and carbonate particles; (b) acid–base reaction and oxidation–reduction potential; (c) basic cations and nitrate ion. Well sampling data collected on the Lake Karachai–Mishelyak River profile in September 1993

for Sr, and 310 for K. Those values are many times (up to three orders of magnitude) greater than the concentrations of the same components in the original technogenic solutions and natural groundwater.

It is fair to say that processes with the same direction will take place as the result of ion exchange reaction, when sodium, dominating in the composition of the

industrial solution (waste), displaces cations of Ca, Mg, Sr, and K from the exchange complex of rock (Rumynin et al. 2005a, b; see also Sects. 20.1.5 and 23.1.2.1). A confirmation to that is the appreciable retardation of sodium concentration wave from the leading front of the concentration waves of Ca, Mg, and nitrate ion (Fig. 15.6c).

The accumulation of alkaline-earth metals in high concentrations in the migrating solution hampers the adsorption of Sr-90. This accounts for the relatively high migration velocities of this radionuclide. On the other hand, the contact of acid replacing and alkaline natural waters (Fig. 15.6b) can be regarded as a kind of moving hydrogeochemical barrier, preventing Sr-90 from reaching the leading zones of the pollution plume. Precipitation of Sr-90 with carbonates takes place on this barrier (Solodov et al. 2005). The migration of Cs-137 has a “non-barrier” character. It is mostly sorbed by secondary and newly formed clayey minerals and ferric iron hydroxides.

Detailed quantitative analysis of such hydrogeochemical processes goes beyond the scope of this work. We will only emphasize here that those processes are largely induced by the hydrodynamics of groundwater flow, a quantitative (model) description of which is given below.

15.4 Overview of Modeling Analysis Approach

Preliminary analysis has shown that migration of radioactive brines is governed by parameters that have not been represented properly by field tests and monitoring data. The plume shape is not consistent with the groundwater flownet, which has been derived from water table monitoring data. The use of mathematical models represents probably one of the very few viable options for matching the gap between our incomplete knowledge of the site and capability of making predictions of future scenarios. Actually, the development of modeling investigations requires:

first, the introduction into the modeling analysis of some strong a priori assumptions. These assumptions may be based on indirect geological-and-structural information as well as on the reconstruction of a hydraulic conductivity profile with the help of borehole logging creating an initial basis for applying more sophisticated 3-D models;

second, the development of a set of alternative models, incorporating different ideas on flow-parameters and geological-and-structural features of the strata. The use of alternative modeling approaches supplemented with sensitivity analyses allows us to establish whether the model simulation can be satisfactory and reliable.

The following assumptions are made in our modeling study:

- (1) The aquifer can be classified as a strongly heterogeneous medium, and a general trend in the transmissivity variation in the plan view can be established on the basis of geostochastic analysis.

- (2) The relief of the aquitard is not flat. The depth of weathering (fractures development) varies in space, i.e., the subsurface interface between the top and bottom zones undulates significantly according to the surface elevation (there are some correlations between the elevations of the surface relief and the subsurface interface). Thus, there are some structural elements in the bottom part of the aquifer that can influence the prevailing brine flow paths but do not affect the regional flow.
- (3) Three zones differing in hydraulic conductivity are distinguished in the vertical direction.
- (4) The storage capacity of the strata is given by both fracture and matrix porosity.

The further differentiation of the modeling approaches is based on some additional conceptual assumptions. First of all, the mass-transport potential is determined mostly by the bulk salt migration. This is characterized by the content of the total dissolved solids and solution density; the concentration of nitrate ion, which dominates in the solution and correlates with its density, can serve as a major non-reactive tracer. Meanwhile, spatial and temporal changes in the concentration of minor species (e.g. radionuclides) do not affect the overall transport potential and can be excluded from consideration. However, the behavior of radionuclides is governed by the concentration of many other dissolved components and complexed species. Therefore, the prediction of radionuclide fate requires the use of reactive-solute transport models. Relevant analyses can be based on either a simplified isothermal approach taking into account the variability of coefficients of equilibrium distribution, or on the basis of a multicomponent approach in the framework of hydrogeochemical coupled models. Physical and chemical processes cannot be properly simulated separately in all cases.

Below we mostly consider the features of migration flow hydrodynamics with the help of mathematical modeling apparatus. The construction of a more general model, taking into account the entire range of the physicochemical interactions considered above is a task of a special study.

15.5 Model Setup and Calibration

The calibration and validation procedures are aimed at the proper identification of different parameters: (1) those governing the bulk flow and solute transport, and (2) those controlling radionuclide retardation. The variables considered are hydraulic head, nitrate concentration, and solution density. Model calibration involves a comparison between some specific simulation results and available field data in order to estimate parameter values. Calibration reliability is significantly enhanced if model results are checked against the mass balance of solutes and flow at the outlet boundary associated with discharge areas. The basic problem of model validation is concerned with assessing whether the assumptions and parameterizations used in the models are consistent with and able to reproduce the observed effects/processes such as advection, dispersion, and the contaminated water–rock interactions. In this

chapter, we focus on parameters governing the bulk flow and brine transport, while those controlling radionuclide transport/retardation will be discussed in another work.

15.5.1 Model Design

The first step of groundwater dynamics and contaminant transport analysis was concerned with the development of a two-dimensional regional flow model (Fig. 15.1). This constituted the domain for studying three-dimensional brine migration in a sub-area (“window” model) selected within the regional modeling domain (Fig. 15.7). This creates a basis for further radionuclide transport analysis and forecasting.

The domain is 10,250 m long, 9,250 m wide, and 100 m high on average. The results obtained from solving the 2D flow problem serve to set the boundary conditions for the designated 3D area. The internal boundaries are associated with surface water bodies and streams (Fig. 15.7a). In constructing the 3D-window model we assumed that six zones of transmissivity could be identified on the basis of a geo-statistical analysis of pumping test data (Fig. 15.7b). The average rate of leakage from the reservoir, $234.5 \text{ m}^3/\text{day}$ (the area of the reservoir’s bottom is $375,000 \text{ m}^2$), was assumed to match the total volume of the brine, $3.4 \cdot 10^6 \text{ m}^3$, released into the aquifer over the 40-year period. The density of the liquid waste was assumed to be 1.07 g/cm^3 .

During the calibration procedure, both variants of vertical homogeneity and heterogeneity of the domain were considered and discussed. According to the main assumption discussed in the previous paragraph, the bottom of the domain, i.e., the subsurface interface between the domain considered and the semi-permeable underlying aquitard, was assumed to be undulating according to surface elevation. Finally,

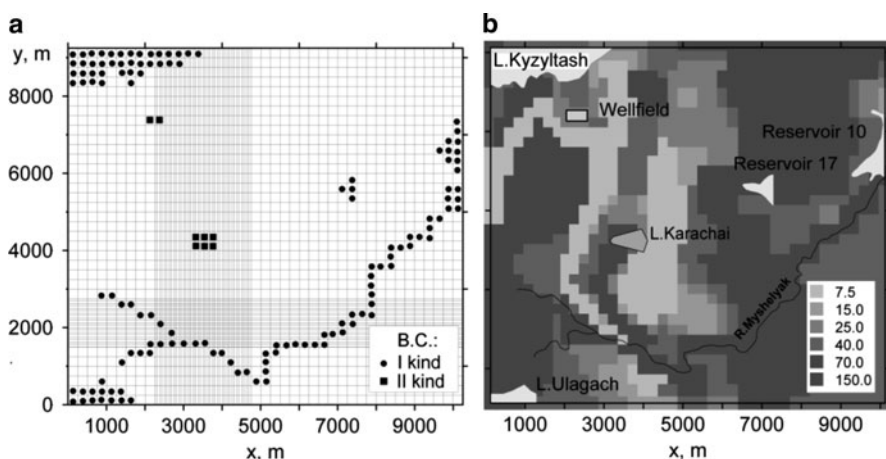


Fig. 15.7 3D modeling domain: (a) discretization of the domain and boundary conditions, and (b) transmissivity distribution (numbers in legend are transmissivity values, m^2/day)

two hypotheses for effective porosity of the model domain were regarded as the basic ones. The first modeling approach assumed fracture porosity ranging between 0.002 and 0.006, which corresponds to rock fracture porosity within the depth interval of 30–70 m (see Fig. 15.3b), where the major salt mass is concentrated. The second modeling series assumed that the matrix porosity is predominant, and therefore the effective solute-accessible porosity can rise up to 1.5% (maximum value).

The calibration of the flow/transport model was based on hydrodynamic and geochemical data (concentration of NO_3^- ion) for groundwater within the contaminated site. Calibration procedures included a correction of the transmissivity field established in the framework of 2D regional modeling to match the observed nitrate concentration contours for 1990. One of the identified local zones with relatively high permeability, extending in the NW–SE direction and lying between the pollution source and the Mishelyak River valley, coincides in space with the Mishalyak fault zone. Based on a priori assumptions, the hydraulic conductivity of fractured rocks in the river valley was taken equal to the maximal value 1.5 m/day.

A set of alternative models incorporating different ideas on flow-parameters and geological-and-structural features of the strata seems to be a viable option for studying the contamination in the Lake Karachai site. In our evaluation, both sharp interface (such as DENSFLOW) and fully miscible liquids (such as TOUGH2) were considered, as described below.

15.5.2 *Sharp-Interface Approach*

The choice of a sharp-interface model for the problem under consideration is motivated by the possibility given by this modeling approach to distinguish preferential flowpaths of brine transport and to estimate parameters governing the interface velocity. In this context, the interface is associated with the core of the plume represented by undiluted brine (Fig. 15.8).

The results indicate that the calculated potentiometric surface of fresh water is in good agreement with field measurements. Also, the shape of the delineated contamination zone is consistent with the shape of the modeled plume body (Fig. 15.8). This supports our confidence in the corrected transmissivity field (Fig. 15.7b) and the recharge rate distribution over the area being close to the actual hydrogeological characteristics of the site. The velocity of the advancing front of the plume for the given transmissivity field is controlled by the effective porosity, which was found to be 1.5%, in close agreement with the sum of fracture and matrix porosity of the domain.

A satisfactory agreement between model and field data can be achieved only when the hydraulic conductivity in this zone lies within 0.3 to 0.35 m/day. Lower values cause more rapid joining of the top surface of intrusion and the water body bed; the values in excess of this range yield too flat contact and a displacement of the leading front of intrusion toward the river that is too rapid to be realistic. The reproduction in the model of high-gradient (in terms of hydraulic head) eastern zone

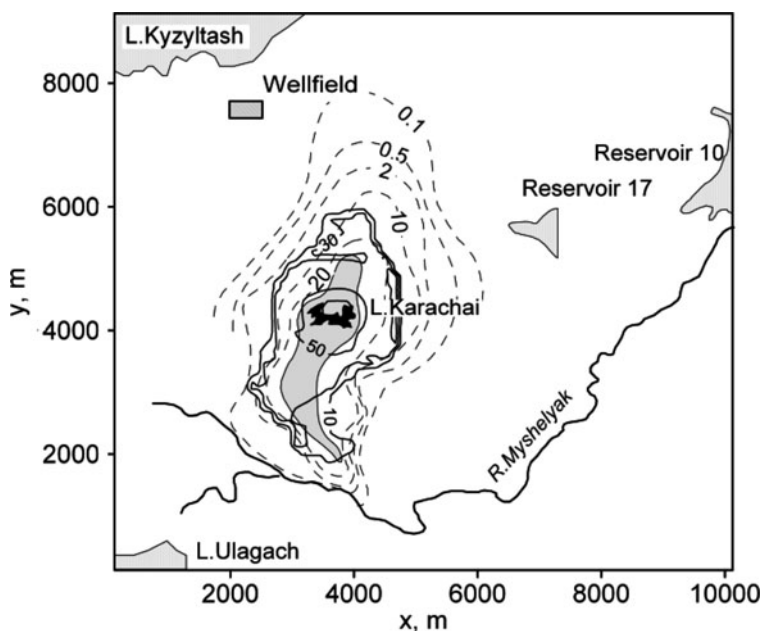


Fig. 15.8 DENSFLOW simulation results of plume spreading at $t = 40$ years. The plume contours (thick solid lines) are thickness of the brine body (m); dashed lines are the observed values of NO_3^- content (g/L), as of 1990 (Drozhko et al. 1997c); dark area is for $\text{NaNO}_3 \approx 50$ g/L.

and the plateau-like area near the pollution source required the hydraulic conductivity to be specified in these domains, $k = 0.075$ m/day. Conversely, the model and real hydroisohypse maps of the western part were made to coincide by including in the model a submeridional linear zone with higher hydraulic conductivity, $k = 1.5$ m/day.

Furthermore, the relief of the aquifer bottom and the structure of soil heterogeneity were confirmed to be the major factors controlling preferential flow paths of the brine movement. The combination of these factors forces the brine to move southwards, toward the river valley (Fig. 15.8). Multivariant modeling assessments have enabled us to draw the following preliminary conclusions:

- (1) After 40 years of brine leakage from the reservoir, the model plume shape and size are consistent with the respective characteristics of the actual plume; the advancing front of the plume is about 0.5 to 1 km from the river valley. We noted that the depth of the water–brine interface is rather sensitive to rock hydraulic conductivity. Thus, the interface location can be used to help the model calibration procedure.
- (2) In the case when the additional capacity contributed by porous blocks is neglected, the simulated plume moves toward the discharge areas with enhanced velocity, which is two to three times the velocity of the actual plume movement.

- (3) Accordingly, an increased value of effective porosity (which is associated, in this case, with the rock matrix) has led to more satisfactory results, i.e., a better agreement between modeling results and observed data. Therefore, we consider these results as a confirmation of the fracture void deficiency for accumulating all the volume of brines within the existing plume's boundaries above the bottom aquitard. Taking into account the matrix porosity as a potential capacity for waste accumulation furnished improved modeling results.

15.5.3 Fully Miscible Transport Modeling Approach

The next stage of modeling was performed using the TOUGH2/EOS7 (Sect. 14.1) simulator. The TOUGH2 code makes use of a numerical scheme (EOS7 module) based on higher-order differentiation methods, which minimize grid effects and the smearing of concentration fronts from artificial (numerical) dispersion. Such methods can provide a high accuracy in modeling solute transport, especially in the case of zero or almost zero physical dispersion.

The window model domain was discretized in the $x-y$ plane as shown in Fig. 15.7a, with 20 blocks in the z -direction (Table 15.3). The horizontal heterogeneity and three homogeneous physical layers (Sect. 15.2) were modeled. Figure 15.9 illustrates the comparison of modeling results with the observation data on nitrate ion distribution. These are in rather good agreement, and the simulated plume reflects the general tendency of the migration process quite well. As expected, the plume reaches the bottom of the aquifer and begins to spread horizontally. The influence of the bottom relief is quite evident (as was found also using the sharp interface model) and the plume tends to spread southwards during the contamination period (Fig. 15.10). The results obtained in the framework of fully miscible approach indicate that:

- (1) both observed and computed plumes are characterized by the presence of a high-density brine intrusion (a “nucleus” of solution body) in the lower part of aquifer. However, some discrepancies in the corresponding maximum values of the nitrate concentration have been found; these differences may be due to numerical dispersion related to the use of a coarse grid for spatial discretization;
- (2) the plume spreading in the southern direction is confined by the drainage effect of the Myshelyak River valley: the contaminated water flux is separated from the area at the right bank of the Myshelyak river.

Table 15.3 Profile model discretization

Number of layer	Top of the layer ^a , m	Percent of permeability, %	Number grid-layers
1	100	30	6
2	70	50	8
3	30	20	6

^a From aquifer bottom

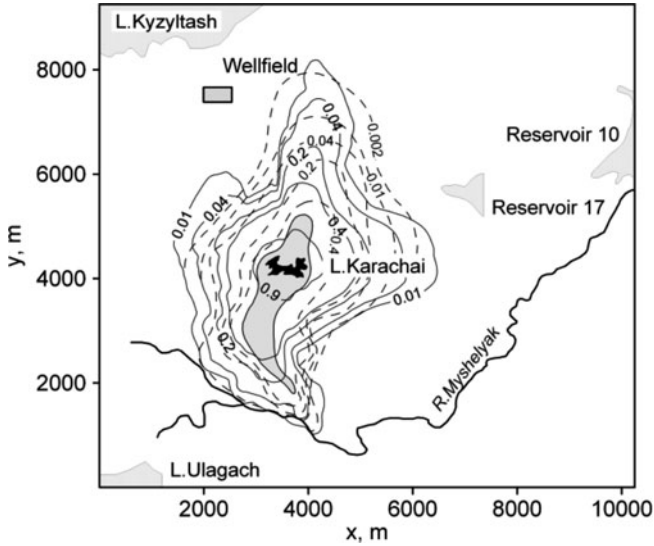


Fig. 15.9 Comparison between simulated (TOUGH2, *solid lines*) and observed (*dashed lines*) contours of concentration distribution within the contaminated site (normalized concentration; sodium nitrate concentration at the source was assumed to be 50 g/L; $t = 40$ yrs (1990))

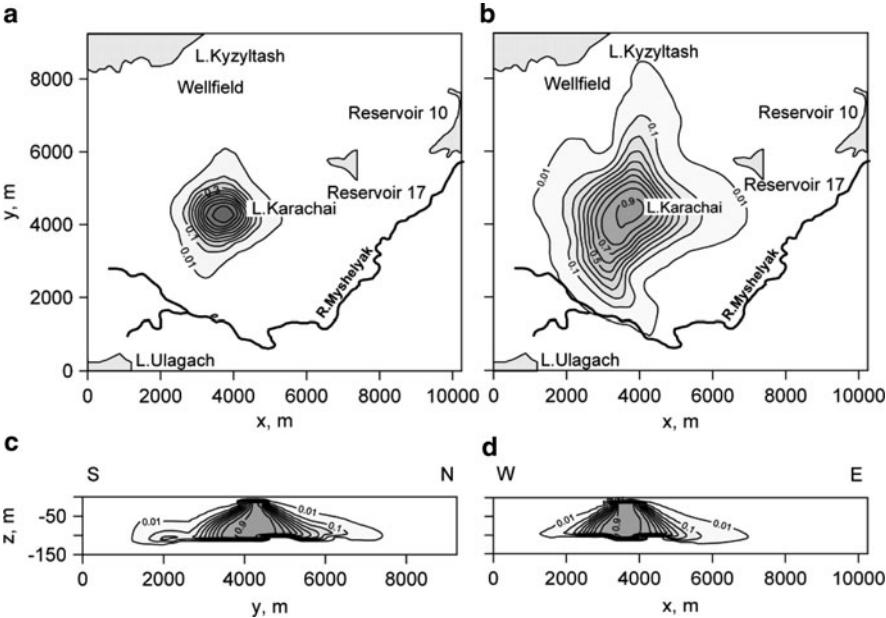


Fig. 15.10 Spatial distribution of salt concentrations (results of TOUGH2, $t = 40$ years). (a, b) Planar view: (a) $z = 15$ m, (b) $z = 90$ m; shown in the bottom is the profile of the plume: (c) N–S, (d) W–E

15.5.4 Brine Plume Simulation and Prediction

As was done during model calibration, the initial runs for simulating density-induced transport at the Lake Karachai site were performed using the DENSFLOW code. Two periods were chosen for the modeling. During the initial stage, namely the first 50 years, the surface reservoir is assumed to be the source of the brine release into the aquifer. The total recharge over this period was assigned to be equal to $3.4 \cdot 10^6 \text{ m}^3$. Another major assumption was that the contamination source is isolated from the subsurface environment and only the rock structure and regional flow govern the plume spreading. Modeling results indicate that:

- (1) the 50-year period after isolation of the source from the subsurface environment is characterized by waste accumulation in the stratum underlying the river valley;
- (2) modeling scenarios for long-term migration (when the plume reaches the river valley, Fig. 15.11) show that there is no interaction between the subsurface plume and the stream (river): the upper flow of infiltrating water discharging into the river protects the surface water from contamination by the heavy brine. Note that such result cannot be obtained in principle with the help of two-dimensional profile models. It implies that the depth of the saltwater layer is less than the total thickness of groundwater flow in the zone of its discharge into the river, i.e., in the case of a frontal dynamics of the process, the top part of the aquifer will be occupied by fresh water (its flow forms due to area-distributed infiltration recharge of the water-bearing stratum).

We are aware, however, that the sharp-interface approach may furnish an excessively optimistic prediction of salt spreading. The model cannot simulate correctly

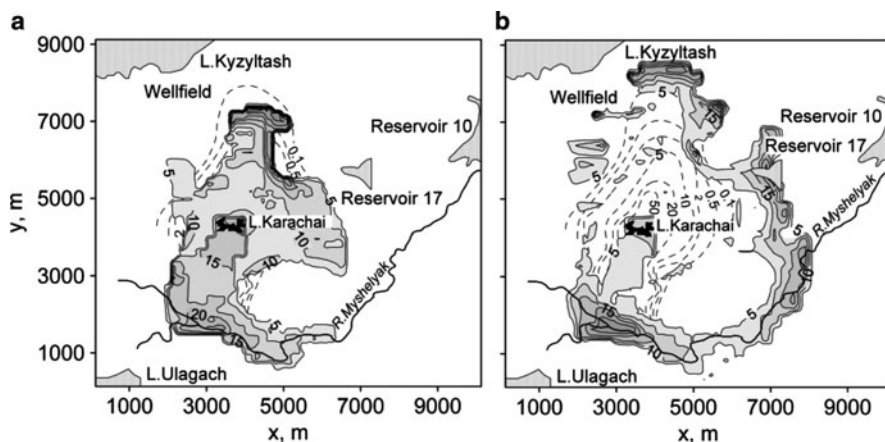


Fig. 15.11 Brine migration scenario simulated using DENSFLOW at (a) $t = 80$ and (b) $t = 120$ years. The plume contours (solid lines) are expressed as the thickness of the brine body (m); dashed lines identify the observed values of NO_3^- content (g/L), 1990

the upward movement of the interface in the area where the vertical hydraulic gradients are noticeable. Furthermore, transverse vertical dispersion may play a role in causing the discharge of low-concentration salty water into the river. This motivated the use of the assumption of full miscibility, as discussed below.

Long-term predictions of brine spreading using the full-miscibility approach were performed using the TOUGH2/EOS7 simulator. After ceasing the contaminant “injection”, the brine continues to migrate preferentially in the southern direction towards the river where it discharges. However not all the brine is predicted to end up in the river, since a weakly contaminated plume (low concentration of nitrate) spreads in the eastern direction, as shown in (Fig. 15.12). Furthermore, a strong cross-section differentiation of the brine concentration due to gravity is evidenced in plotting brine concentration along vertical sections of the domain.

In conclusion, we will consider in more detail the role of the storage capacity of the relatively impermeable bed of the water-bearing stratum. The schematization of hydrogeological conditions in all studies known to the author supposed an absolute aquiclude to exist near Lake Karachai at depth of 100 m from the day surface, and the bottom (no-flow) boundary of three-dimensional grid models was commonly associated with this aquiclude (Petrov et al. 1994; Rumynin et al. 1998). In this context, it is of interest to evaluate the errors appearing when the permeability (weak as it is) of the impermeable bed in the given area is neglected.

Calculations using a conceptual numerical model (the model domain approximately corresponded to the scale of the pollution process described) have shown

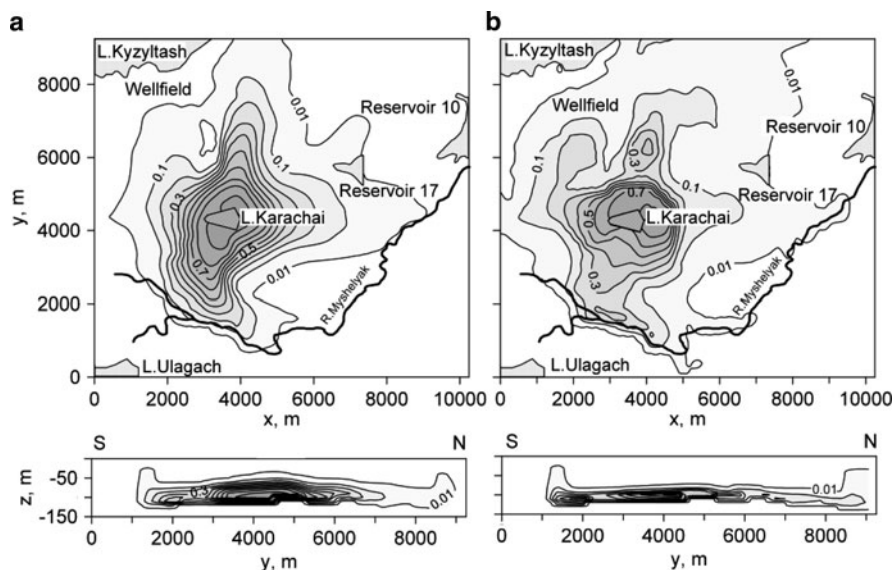


Fig. 15.12 Plume spreading (plan view, $z = 80\text{m}$ below the surface) simulated using TOUGH2 at (a) $t = 80$ years and (b) $t = 160$ years. Plume contours are expressed as normalized concentration of brine

(Rumynin et al. 1998) that the flow of salts due to leakage of dense solutions from the surface basin can embrace not only the top (100-m) part of the section represented by high-permeability rocks, but also deep zones of the fractured massif, which are conventionally assumed to be impermeable ($k < 0.01$ m/day). Because of the effect of gravitation-induced spreading of salt water, the volume of polluted waters in such zones can be comparable with the appropriate characteristic for the upper part of the section or even appreciably exceed it. Therefore, the values of the lateral components of the mass flux in the high- or low-permeability rocks prove to be comparable.

Unfortunately, monitoring observation data for the area under consideration characterize the distribution of salts only in the top 100-m zone. The situation resembles the description of the top, above-water (visible) part of an *iceberg*, while its under-water part, which governs the drift velocity, remains beyond the scope of the researcher. The interpretation of the appropriate hydrochemical observations, neglecting the accumulating role of underlying, low-permeability, effusive formations (a relative aquiclude) may lead to an erroneous opinion about the parameters governing the process. In particular, the coordination of model and field data on the plume drift velocities in the horizontal direction requires one to specify knowingly overestimated values of the aquifer effective capacity (fracture porosity) in the initial (100-m) aquifer model. Such porosity can be misinterpreted as a manifestation of dual porosity of the medium.

Overall, the analysis carried out above shows that the mobility of radionuclides that are conventionally classified as well-adsorbable becomes very high in systems with a high content of inorganic salts, thus dramatically increasing the hazard of radiation impact on the environment. The prediction of radionuclide behavior in the composition of concentrated salt solutions is the problem of higher complexity, whose solution implies the joint use of hydrodynamic and physicochemical methods of numerical modeling.

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Chapter 16

Modeling of Seawater Intrusion in Coastal Area of River Andarax Delta (Almeria, Spain)

The problem of groundwater quality preservation in coastal regions faces almost all countries that have marine water areas, in particular, insular states. This problem is aggravated by the fact that coastal areas are commonly most habitable and industrially developed, and groundwater serves as a major source of drinking water supply to the population. Indeed, freshwater resources in the coastal aquifers are likely to experience disastrous and irreversible impacts due to overexploitation and ingress of seawater into freshwater aquifers. The latter process leads to a decrease in groundwater quality at water supply systems located within the coastal areas. Therefore, the management of groundwater resources in coastal aquifers requires special attention to minimize the extent of seawater intrusion into aquifers and upconing of seawater near pumping stations. Numerical modeling that treats density-dependent flow and miscible salt transport (Bear 1999; Zhang et al. 2004; Gingerich and Voss 2005; Giambastiani et al. 2007) can help in creating a basis for the relevant hydrogeological investigations and forecasting. This section is an example of model analysis of seawater intrusion into coastal aquifers, which naturally discharge into the Mediterranean Sea at a resort coastal zone in Almeria province (Spain).

16.1 Study Area

The hydrogeological conditions in the Andarax River delta, where groundwater flow discharges into the Mediterranean Sea (Fig. 16.1) include a marine intrusion that affects groundwater quality in coastal aquifers. The active development of these horizons by water intake wells (and water withdrawal from shallow pits) started in the 1960s. Almost immediately, this caused a decline in the pumped-out water quality, which is due to the northward replacement of the natural seawater–groundwater interface and the subvertical pulling of a saltwater wedge toward water intake wells. The progressing salinization of horizons was a cause of an appreciable decrease in the volumes of withdrawn water.

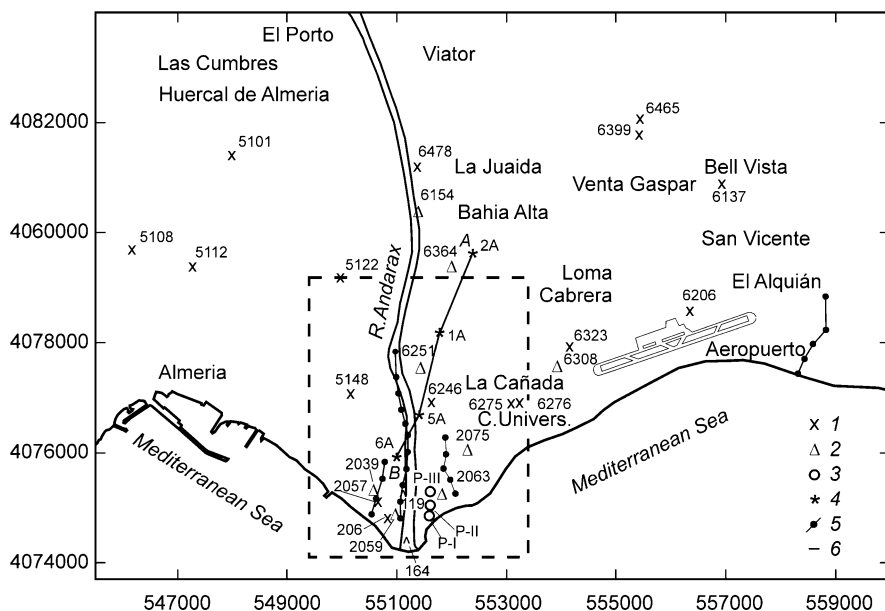


Fig. 16.1 Schematic map of the study area. (1–2) Pump-out wells: (1) with occasional measurements of water quality, (2) with available data on water chemistry variations over time; (3) observation wells where the distribution of water conductance over depth has been studied; (4) exploratory wells with hydrochemical data on individual intervals; (5) VES profiles; (6) section line A–B; dashes outline the model domain (rectangle)

16.1.1 Brief Geological Description of the Site

The geological structure of the territory includes the following sediments and rocks (Fig. 16.2) (Atlas... 1998; Gisbert et al. 1999; Martos 2001).

1. A complex of sediments represented by channel deposits, Quaternary deltaic fluvial and marine deposits (sand, pebble, and gravel with rare seams of clay and loamy material); the thickness of deposits varies here from 80 to 90 m in the central part of the basin to a few meters in its periphery.
2. A complex of sedimentary rocks of Pliocene–Quaternary ($N_2^3 - Q$) and Pliocene (N_2), represented by conglomerates, marl with numerous seams of sand and gravel; two complexes are identified in the Pliocene rocks: “marine” facies dominate in the bottom part of the basin, while on the margins of the basin, it is represented by a sand stratum, which is replaced by marls and yellowish sand-clay marls (with “lepra”); their thickness varies from several meters at their margins to several hundreds meters in the center of the basin; the “continental” facies includes deltaic deposits with different lithology and the predominance of conglomerates, sands, and silts, whose total thickness can reach 200 m.

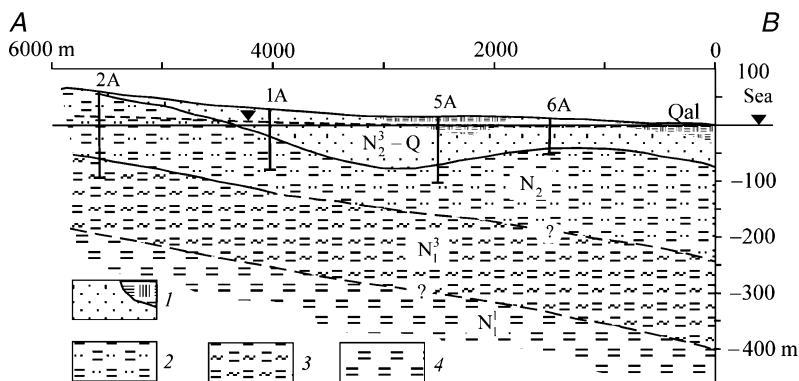


Fig. 16.2 Schematic geological–hydrogeological section along A–B line (Fig. 16.1). Deposits: (1) Quaternary and Pliocene–Quaternary deltaic and alluvial; (2) Pliocene (marls and conglomerates with sand seams); (3 and 4) Upper and Lower Miocene (marls with relatively rare seams of sand–clay material)

3. The Upper and Lower Miocene deposits ($N_1^3 - N_1^1$), are represented by marls with relatively rare seams of sand–clay material; the deposits are intersected by very few wells and are poorly known; their thickness can reach several hundreds of meters. No contact was found to exist with the underlying Triassic (T_1) and Permian (P_1) deposits.

16.1.2 Hydrogeological Setting

The main aquifer system is associated with *Quaternary* (alluvial and deltaic gravel and sand with rare clay and silt seams) and *Pliocene–Quaternary* deposits (conglomerates, sands, sand loams, and clays). The alluvium is “inserted” in the Pliocene–Quaternary deposits with close hydraulic interaction existing between them. Alluvium thickness at the Andarax River mouth reaches 80–90 m. Two aquifers are identified near the delta: a top, unconfined one with the mean thickness of 25 m, and a bottom, low-head one with lower permeability and a thickness of up to a few tens of meters. The total transmissivity of the aquifer system varies from 350 to 1,200 m²/day, and the specific discharges of wells vary from 1 to 20 L/(s m). The deltaic deposits on the left bank of the Andarax River have an appreciably greater permeability than those on its right bank.

The underlying aquifer is associated with *Pliocene* deposits. The water-bearing rocks are sand and conglomerate seams in a marl unit, whose thickness may reach 150 m. The mean transmissivity of the aquifer is several hundreds of square meters per day, though it can be as large as 1,500 m²/day in some areas.

The aquifer of *Upper Miocene* deposits is lithologically similar, though the occurrence of permeable sand seams is less, resulting in an appreciably lower transmissivity. This aquifer is poorly known hydrologically.

The *Lower Miocene* stratum can be considered as a regional aquiclude.

In the Andarax River delta, the top aquifer is directly recharged by river water during floods, and groundwater levels rapidly recover in this period. Deeper beds (the second aquifer) are recharged at the entry of the stream underflow into the delta. Additional recharge is due to the area-distributed infiltration of atmospheric precipitation and losses of waters used for irrigation. The infiltration recharge does not exceed 15 mm/year. Lateral recharge from the side of the Sierra de Hador is also possible. The major portion (up to 65%) of safe groundwater yield are associated with this aquifer. Well yields reach 15–20 L/s. The total water withdrawal varies from 8,200 to 13,700 m³/day. The submarine groundwater discharge is estimated at values from 2,700 to 5,400 m³/day.

Analysis of the many-year evolution of groundwater piezometric surface (Fig. 16.3) shows that the intense development of the coastal aquifer system in the 1960s–1980s has caused the formation of a depression surface in the coastal zone: the absolute elevations of groundwater level in the center of depression dropped 2–3 m below the reference sea level (Bosch et al. 1997). This contributed

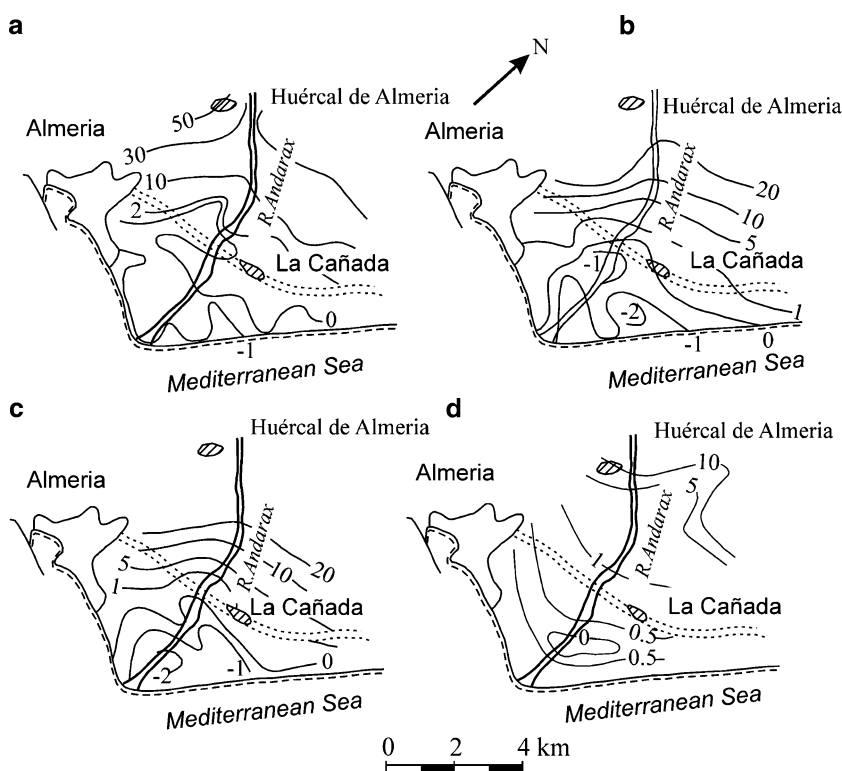


Fig. 16.3 Evolution of piezometric surface (contour lines show the distribution of heads, m). (a) October 1975, (b) April 1985, (c) April 1989, (d) May 2002

to the shoreward displacement of intrusion and salinization of groundwater. In the late 1980s, the rate of water withdrawal decreased and groundwater levels in the coastal zone rose to the elevations close to ± 0 m.

Analysis of hydroisohypse maps shows that groundwater table within the 1–2-km coastal zone lies near ± 0 m. This, in particular, suggests a very weak discharge of groundwater flow into the sea. However, the elevation of the level is negative in some points. The hypsometric surface slightly rises northward, reaching the elevation of $(+12)–(+16)$ m.

16.2 Groundwater Salinization

The quantitative estimation of the effect of seawater intrusion on groundwater quality in the coastal zone of the Andarax River delta was based on information that can be divided into several categories (see Fig. 16.1). (1) Data of sampling separate (commonly one or two) well intervals. (2) Results of periodic analysis of water samples taken from water intake wells; the wells for which such data are available can be divided into two groups: (a) the wells for which water chemistry was determined over at least 3–4 years and (b) wells sampled a limited number of times during less than 3 years. Overall, 32 observation and pumping wells were identified in the study area. The salinity of collected groundwater samples was measured in the laboratory. (3) Data on the distribution of salt content over depth obtained by electrical logging of wells. (4) Data on the freshwater/saltwater interface collected by VES method during geophysical studies.

Our analysis was mostly based on the results of studying the conductance of samples and their content of chlorine (Cl^-) and sulfate (SO_4^{2-}) ions. Water salinity (C , mg/L) was approximately estimated from its electrical conductivity (σ , $\mu\text{S}/\text{cm}$) as

$$C = (\sigma - 522)/1.11.$$

Unfortunately, as it was mentioned above, the depth of wells drilled in this area rarely exceeds 100 m; therefore, only the top part of the water-bearing stratum, confined to Quaternary and Pliocene–Quaternary deposits, was studied hydrochemically. The occurrence of salt seawater in the bottom part of the section can be judged only by electrical survey data.

16.2.1 Spatial and Temporal Changes in Groundwater Quality

Analysis of the effect of marine intrusion on groundwater is complicated by the fact that the natural groundwater in this region have higher background concentrations of the major marker anions Cl^- and SO_4^{2-} (Fig. 16.4); this is due to the dissolution of gypsum-containing rocks in the upper and middle reaches of the Andarax River

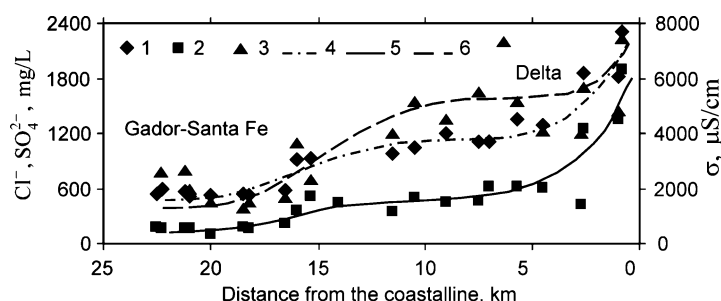


Fig. 16.4 Variations in water quality in the direction from Santa Fe toward Andarax River delta. (1) Electrical conductivity, (2) chlorides, (3) sulfates, (4–6) trends for 1–3

(Martos 2001) and the continental salinization of salts. In the further analysis we will use the following values to characterize groundwater composition in the top zone of the section at the southern boundary of the Andarax River delta (natural background levels): $C = 2.5\text{--}3.0\text{ g/L}$ (TDS; this value corresponds to $\sigma = 3,000\text{--}4,000\text{ }\mu\text{S/cm}$), $C_{\text{Cl}^-} = 450\text{--}500\text{ mg/L}$, and $C_{\text{SO}_4^{2-}} = 1,400\text{--}1,500\text{ mg/L}$ (this number corresponds to about 50% of seawater sulfate content). Interestingly, sulfate concentrations are appreciably (2.5–3 times) greater than those of chlorides. An inverse relationship $C_{\text{Cl}^-}/C_{\text{SO}_4^{2-}} \approx 7.1$ with concentrations in mg/L is typical of seawater.

Basing on these approximate values and given the ionic composition of seawater, one can approximately estimate the proportion of its mixing with groundwater and evaluate the extent of the domain of intrusion influence on groundwater in the top horizon. Thus, we find that (1) the presence of sea salts in the top part of the section is recorded at a distance of up to 3.5 km from the shoreline; (2) seawater concentration in water intake wells at a distance of 1–1.5 km from the shoreline can reach 12%; (3) the degree of seawater dilution by fresh groundwater increases upstream to 7%.

As can be seen from Fig. 16.5, the freshwater stream underflow in the Andarax River dilutes the intrusion in the central part of the domain under study. In the coastal zone, as well as west and east of the river channel, water salinity (C calculated from σ) varies from 2.5–2.7 to 8.5 g/L; chloride concentrations increase from 500 to 2,000 mg/L.

Resistivity survey was carried out at monitoring wells P-I, P-II, and P-III (Fig. 16.6), located within about 200–400 m from the shoreline, Fig. 16.1 (Gisbert et al. 1999). It can be readily seen that the interface between salt seawater ($C = 42\text{--}46\text{ g/L}$) and low-salinity water ($C \cong 6.7\text{ g/L}$) lies at depth 30–40 m from the surface. In all appearance, the main intrusion of salt seawater takes place in the bottom part of the section, represented by Pliocene rocks. The salinization of the top part of the section takes place under the effect of dispersion processes and is stimulated by water intake through wells. The latter process causes the pulling (rise) of saltwater near water intake wells.

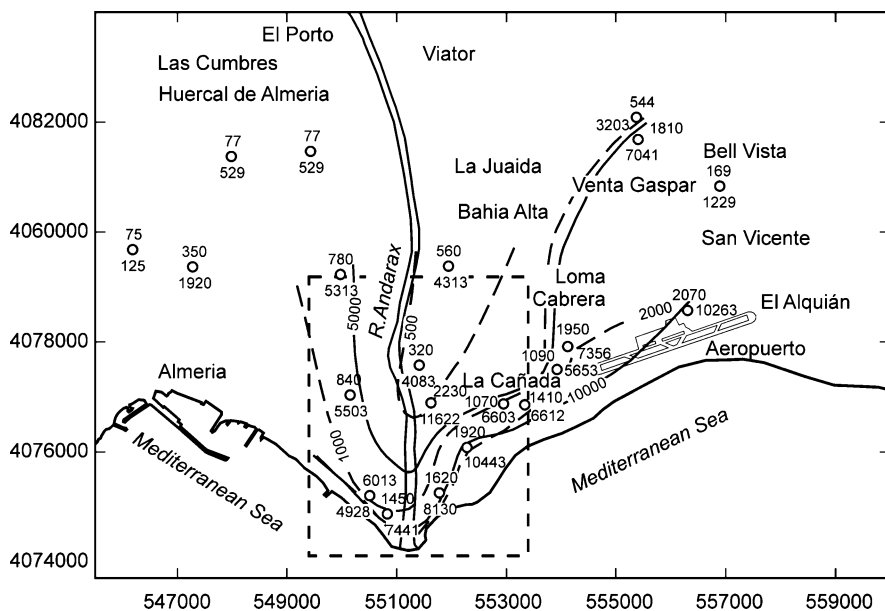
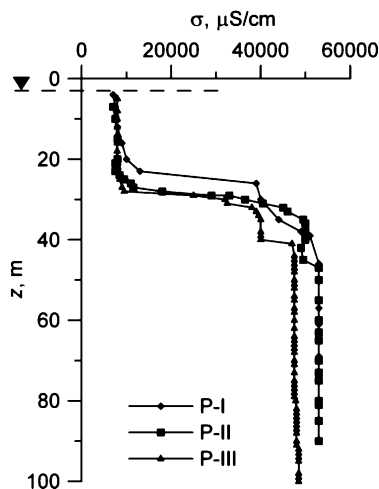


Fig. 16.5 Contour lines of chloride concentration (*dashed lines*, mg/l) and electrical conductivity (*full line*, $\mu\text{S}/\text{cm}$). Circles show wells (the top number is chloride content, the bottom number is electrical conductivity)

Fig. 16.6 Variations in electrical conductivity over depth in wells P-I, P-II, and P-II



Analysis of the available data on wells 6308, 2039, 6154, 2059, 2075, 2063, and 6251 (see Fig. 16.1) showed that in period 1982–2004, groundwater chemistry varied slightly within the salinization zone. This means that the progressive deterioration in water quality took place in earlier periods, for which there are no reliable

data. Some regular trends were recorded only in two wells – 2063 and 2039 (years of 1997–2000), where the salinity and chloride concentration dropped one and half times clearly due to a decrease in water intake in that period.

16.2.2 Major Results of Vertical Electrical Soundings

The vertical electrical sounding (VES) method is usually considered for the sub-surface investigation of geologic environments consisting of horizontal or nearly horizontal layers, such as occur in unconsolidated sedimentary sequences. VES can be also recommended for salinity mapping of coastal groundwater aquifers (Stewart 1999).

At the River Andarax site, apparent electrical resistivity (ohm-m) was measured using VES technique in four profiles at 25 locations within the costal area (Fig. 16.1). VES were carried out by using an asymmetric “MNAB” apparatus with maximal spans OA 680 and 260 m, MN = 1, 20, 100 m. Equipment with the operating frequency of 4.88 Hz was used for electric sounding.

VES profiles were used to establish the position of the nucleus and the affecting zones of seawater intrusion. The penetration distance of intrusion into the continent, recorded by electrometry, was 500–1,000 m at depth of 120 m. Hydrogeological sections along two (1 and 2) profiles, obtained by VES interpretation, are given in Fig. 16.7. Experimental plots were used to convert the specific resistance of rock to the mineralization of seawater saturating it. The main result of geophysical studies

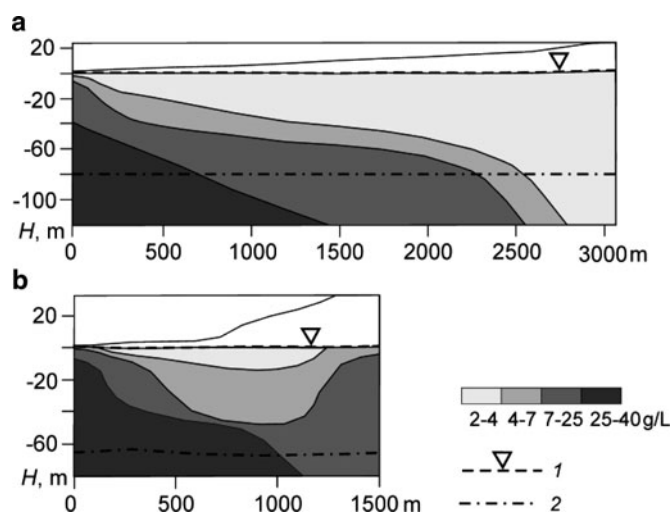


Fig. 16.7 VES data interpretation results for profiles (a) 1 and (b) 2. (1) Groundwater table, (2) assumed marl boundary

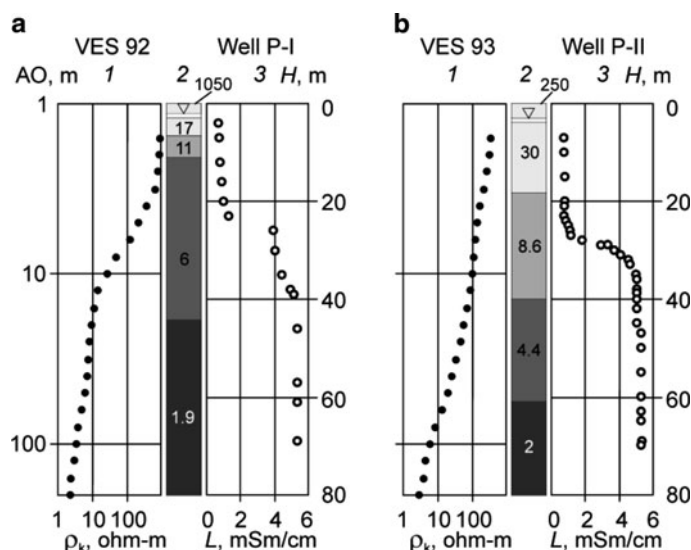


Fig. 16.8 Comparison of hydrogeological interpretation of VES data (point nos. (a) 92 and (b) 93) with conductometry data of nearby wells P-I and P-II. (1) VES curve, (2) geoelectrical section with the specific resistance of layers in ohm-m (depth scale is on the right), (3) well conductometry curve

in the coastal area was the determination of the depth to the top part of seawater intrusion (Figs. 16.7 and 16.8). Again, intrusion dilution zone at depths of 80–120 m was outlined. The effect of seawater intrusion in this depth interval disappears at a distance of 700–2,500 m from sea shore.

16.3 Conceptualization and Model Design of Seawater Intrusion Process

The structural scheme of model domain is given in Fig. 16.9. In the vertical section, this model has three layers (Fig. 16.10): the top layer is associated with unconsolidated Quaternary and Pliocene–Quaternary deposits ($N_2^3 - Q$); they are underlain by less permeable Pliocene rocks, whose water-conducting zones are represented by sand and conglomerate layers in a marl unit; a less permeable layer of marly deposits with rare seams of water-conducting rocks of Upper Miocene is located further below (N_2^3). Marls of the Middle and Lower Miocene (N_1^1) serve as a floor of the water-bearing stratum.

The rocks composing the Andarax River delta form a trough-type structure: the thickness of layers (aquifers) is maximal in the central part of the delta; it decreases westward and eastward along the shoreline, as well as away from the shoreline.

Fig. 16.9 Schematic three-dimensional representation of a part of the Andarax River delta (the broken line is the line of geological section, Figs. 16.1 and 16.2)

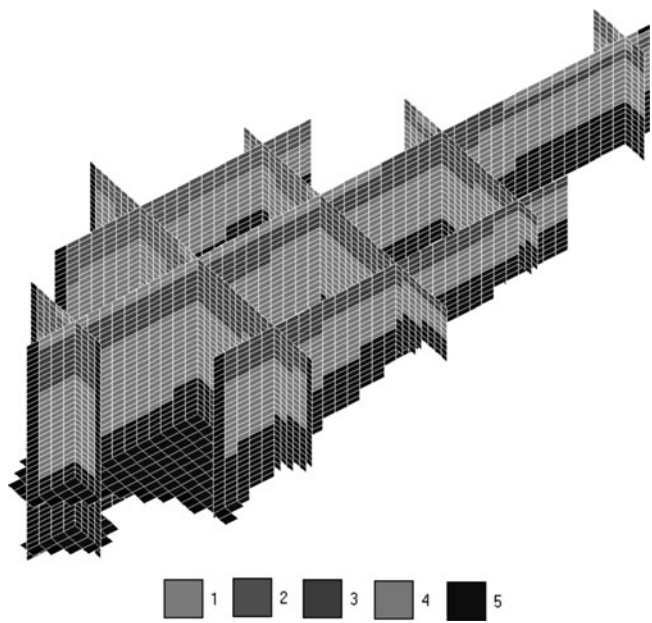
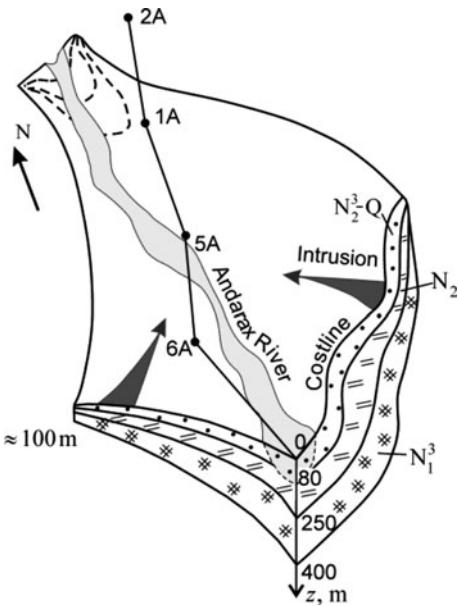


Fig. 16.10 3D fence diagram of the model domain (with “excluded” grid-blocks) displaying interpolated geological layers. (1) Alluvial deposits of the Andarax R. valley; (2, 3) Quaternary and Pliocene–Quaternary deposits (eastern and western parts of the Andarax R. delta); (4) Pliocene deposits; (5) Miocene deposits

Table 16.1 The thickness of hydrogeological units (horizons), m

No. of horizon	Discharge area			Recharge area
	Central part	Western part	Eastern part	
1	80	40	20	40
2	170	60	40	60
3	150	60	40	80

This feature of the structure of the domain was accounted for in the model by varying the absolute elevations of the roof and floor of layers: $Z_{b,t}^N = f(x, y)$ ($N = 1, 2, 3$ is the number of the geological layer, b, t are indices of the floor and roof).

To correctly describe the undulations of roof and floor elevations of geological layers (and thus, their thicknesses, Table 16.1) with appropriate detail on an orthogonal grid, the domain was represented by 40 model layers (Fig. 16.10). The fine vertical partition of the model domain made it possible also to correctly simulate the migration of different-density solutions (Rumynin et al. 2002). In the planar view, the domain was divided into square blocks 100×100 m. The model grid contained 40 blocks in the sublatitudinal direction (x) and 51 block in the submeridional direction (y).

A first-type boundary condition with an absolute elevation of the head of $+12$ m was specified at the inlet boundary of fresh groundwater flow. The initial pressure distribution with allowance made for seawater density was specified in the vertical direction along the shoreline. Hydrodynamically, the lateral boundaries were specified along streamlines and assumed impermeable.

The top horizon was assumed to have a heterogeneous permeability distribution with three zones differing in the hydraulic conductivity (k , m/day): $k = 10$ in the Andarax R. valley, $k = 2$ west of the valley, and $k = 4$ east of it. The second and third aquifers were assumed homogenous (considering the lack of reliable data) with $k = 2$ in the second layer and $k = 0.1$ in the third layer.

The porosity of Quaternary and Pliocene–Quaternary unconsolidated rocks is 25%, and the porosity of Pliocene and Miocene deposits varies from 7% to 5% (considering the saturation of the porous matrix with brines), respectively.

Two zones with different rate of groundwater infiltration recharge (ε , m/day) were identified within the model domain: (1) the central zone, connected with river valley, $\varepsilon = 1.5 \cdot 10^{-4}$; (2) western and eastern, $\varepsilon = 8.0 \cdot 10^{-5}$ (with allowance made for water losses for irrigation).

Well flow rates were specified in accordance with the water withdrawal schedule. Two stress-periods were identified. The first (1965–1989) accounted for the period of most active water withdrawal, when the total yield of wells reached $15,000 \text{ m}^3/\text{day}$, and the second period (since 1990) corresponded to a “soft” water intake regime with a mean rate of around $10,200 \text{ m}^3/\text{day}$.

TOUGH2 numerical simulator (Sect. 14.1) was used for the joint (conjugated) solution of the flow and transport problems in unsteady-state formulation. The part of the model domain that was represented by inactive blocks was excluded from the calculation procedure (Fig. 16.10). This allowed us to reduce the number of model blocks by almost three times (to 27,346), thus decreasing the processor time.

16.4 Modeling Results

To determine the initial position of freshwater–saltwater interface (before the start of development of the coastal aquifer), a stationary problem ($t = 10,000$ years) was solved. The obtained solution of the stationary problem was taken as the initial condition for the subsequent model estimates.

At the *first stage* of the study, a backward estimation period (1963–2002) was considered. The map of pressure distribution shows the formation of local depression cones with a maximal pressure differential with respect to sea of 5,200 Pa (as of 2002), which corresponds to the head of about 0.5 m below sea level. These data are in good agreement with observations of the real head distribution. The drawdown at the maximal water intake (until 1990) was 1.35 m.

The salinization character of the top water-bearing stratum can be judged from maps given in Fig. 16.11. These maps reflect an increase in water salinity (in relative units) with respect to the initial (background) state that existed before ground-water development was launched in the Andarax River delta. The concentration contours are given in dimensionless form (relative to the total seawater salt content $C_0 = 38$ g/L), i.e., to pass to absolute values, one needs to multiply the dimensionless values by C_0 . It can be readily seen that seawater pulling caused an increase in water salinity, mostly in wells located within 1.5–2.0 km from the shoreline. The picture observed in this case is heterogeneous. The zone adjacent to the Andarax R.

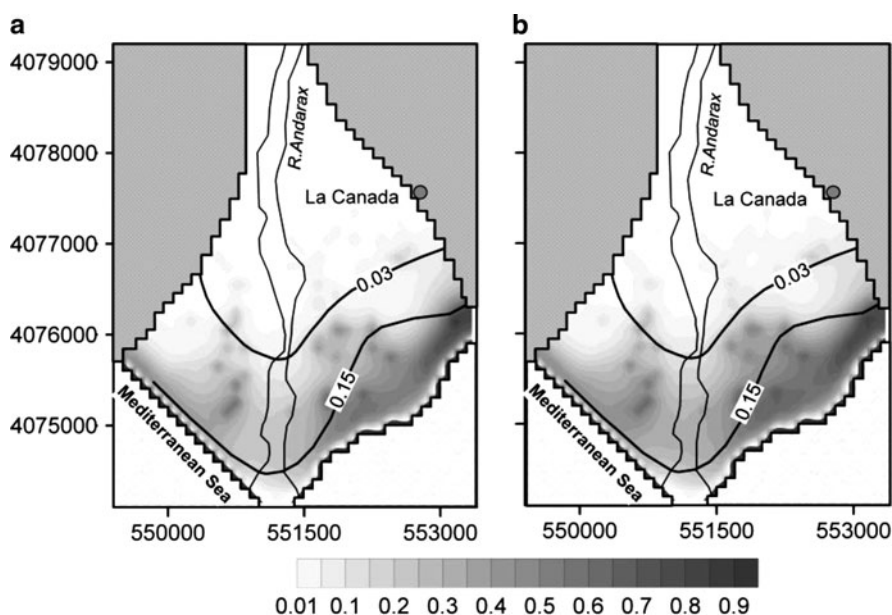
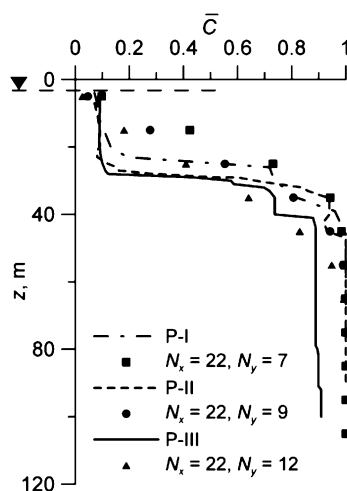


Fig. 16.11 The excess of relative water salinity above background salinity values in the third model layer. (a) After 27 years of operation, (b) after 40 years of operation. Contour lines are relative salinity values according to field data (see Fig. 16.5). Grey shades show the relative ground-water salinity. Hereafter, the geographic coordinate system is given in m

Fig. 16.12 Comparison of modeling data (TOUGH2) with measured distribution of water salinity over depth in wells P-I, P-II, P-III. The relative values are calculated from electrical conductivity – see formula at $\sigma_0 = 53,000 \mu\text{S}/\text{cm}$. N_x , N_y are the numbers of model blocks corresponding to well locations



valley experiences lesser salinization because of the concentration of freshwater flow in the most permeable alluvial deposits. Conversely, local salinization plumes were found to exist near the pump-out well because of the subvertical pulling of seawater toward these wells.

The data presented here are in good agreement with field observations. Thus, Fig. 16.11 gives contour lines of relative mineralization of 0.03 and 0.15 (3% and 15%) drawn based on water conductance measurements (Fig. 16.5):

$$\bar{C} = (\sigma - \sigma^0) / (\sigma_0 - \sigma^0);$$

here σ is the current value of electrical conductivity (for plots in Figs. 16.11, 16.13, and 16.14, these are contour lines of 5,000 and 10,000 $\mu\text{S}/\text{cm}$), σ^0 is the background value ($= 3,500 \mu\text{S}/\text{cm}$), σ_0 is seawater electrical conductivity ($\approx 53,000 \mu\text{S}/\text{cm}$). These contour lines do not much differ from the calculated ones.

An important confirmation of the correctness of the model calculations is the good fit (Fig. 16.12) of the calculated salinity values in the profile to salt distribution over depth in the location points of wells P-I, P-II, and P-III (see Fig. 16.8). It should be mentioned, however, that field observations give somewhat more contrast (abrupt) transitional (dispersion) zone, which is due to the numerical dispersion in the model solution.

The *second stage* of the study involved the analysis of forecasts for three scenarios: (1) the development of the aquifer will continue with the same rate; (2) well yield will be reduced by half relative to the year of 2002; (3) all wells will be stopped, and the duration and the rate of natural rehabilitation of the aquifer will be evaluated.

Figure 16.13 shows the steady distribution of aquifer salinization fields (the second model layer, the occurrence depth is 20 m). Such distribution will establish after about 500 years. It can be seen that with the current rate of water withdrawal

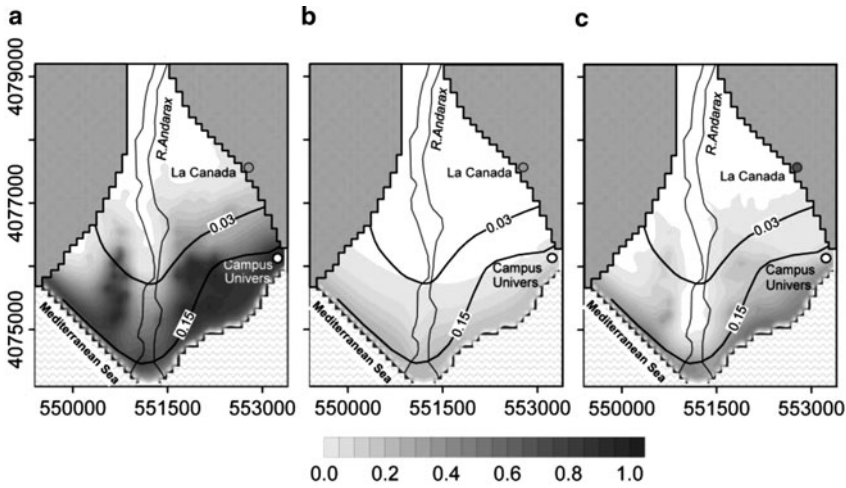


Fig. 16.13 Predicted steady distribution of salinity (relative to background level) for the three scenarios. (a) 1, (b) 2, (c) 3

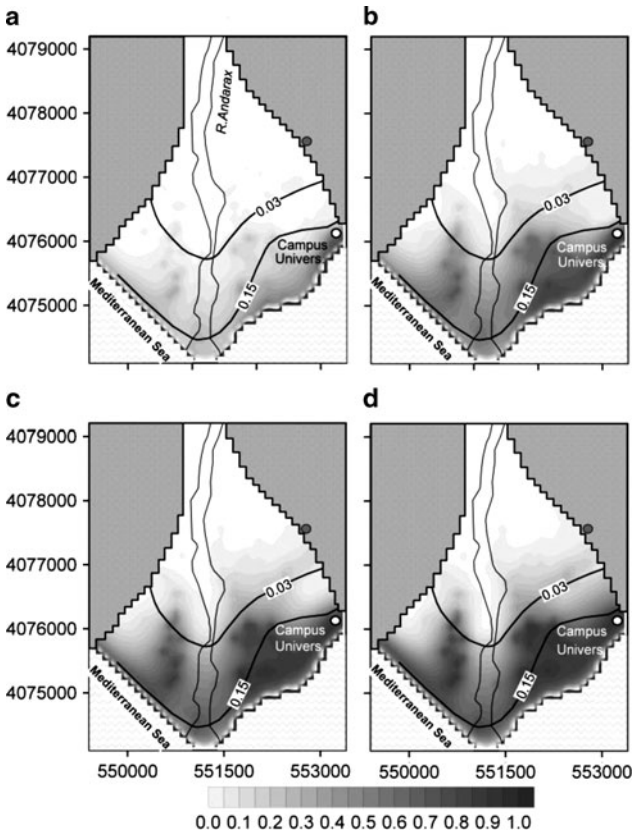


Fig. 16.14 Predicted salinization of groundwater (the 1st scenario). (a) $t = 75$, (b) $t = 122$, (c) $t = 205$, (d) $t = 388$ years from the start of aquifer development

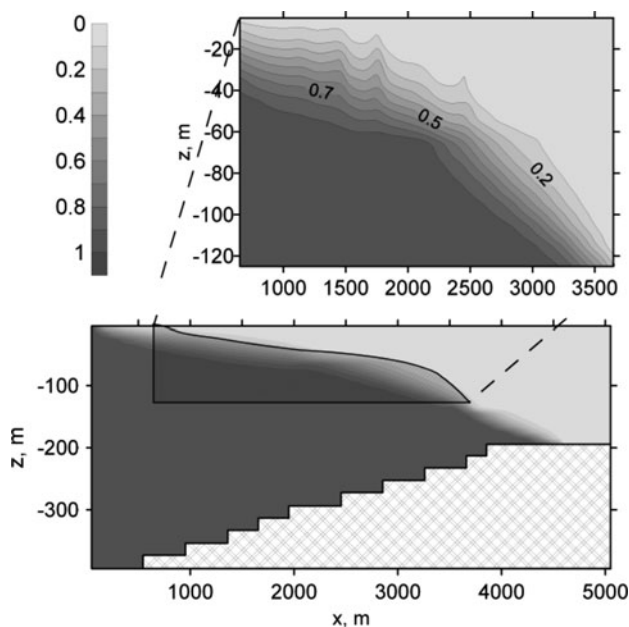


Fig. 16.15 Comparison of the position of the saltwater wedge, determined by using VES data (profile 1), with the results of modeling by TOUGH2 program. The *hatched zone* is the saltwater wedge by VES data

(Fig. 16.13a), the top zone of the section will be salinized to 35 g/L within 3 km from the shoreline. The only exception will be the zone of seawater freshening along the Andarax River. Once the development of groundwater is ceased, the water-bearing system will become much fresher in its upper part (Fig. 16.13b). However, the return of the system to the “initial state” is a long process, lasting for many decades, the fact that is in agreement with the results of such model studies that have been carried out in other regions (Gingerich and Voss 2005). Finally, water intake with 50% intensity is optimal, since a considerable excess of salt concentration against the background is observed only in a narrow coastal zone (Fig. 16.13c).

The general character of salinization evolution over time is illustrated by Fig. 16.14 for the first scenario. It can be readily seen that merging (superposition) of salt water cones that form due to pulling near individual wells takes place over time.

Finally, we call attention to the fact that modeling results are generally in good agreement with the data of electrical exploration (see Sect. 16.2.2). This is especially well seen in the profile passing along the Andarax River valley (Fig. 16.15).

Thus, the study described above shows the potentialities of application of mathematical modeling in making management decision to monitor and control seawater intrusion and planning of groundwater development in the study area. At the same time, the efficiency of geophysical studies in examining marine intrusions is proved.

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Chapter 17

Studying and Modeling of Uncontrolled Discharge of Deep Brine into Mine Drainage Systems at the Korshunovsky Iron Ore Mine (Eastern Siberia, Russian Federation)

A large number of case studies related to mining areas demonstrate that extensive mining activities may affect the groundwater chemistry by lowering the base drainage level and promoting the upconing of brackish groundwater contained in deeper layers of groundwater systems in upper freshwater aquifers (Sherwani 1980; Banks et al. 1997; Mironenko and Rumynin 1999; Nonner 2002). First of all, the upconing process influences the quality of the pumped water. Salinization of well systems and drainage water arises many acute environmental problems in mining areas. Thus, the discharge of highly mineralized mine water into streams deteriorates downstream water quality dramatically.

Earlier, in Sects. 12.3 and 14.2, idealized models were used to analyze the salt-water upconing mechanism below a pumping well, and to determine the salinity of the pumped water. However, there are several natural and artificial factors that result in a disagreement between the actual (observed) behavior of the subsurface migration process and that predicted by the considered conceptual models. Upper aquifer salinization is most sensitive to aquifer heterogeneity, areal recharge distribution, boundary conditions, and the presence of a transition dispersion zone between saltwater and the freshwater extracted by water supply or drainage systems. The experience in the development of the Korshunovsky iron ore mine (Boronina and Rumynin 1999; Mironenko and Rumynin 1999) can serve as an illustration of the peculiarities of salinization of near-surface horizons caused by saltwater upconing and the difficulties in prediction estimating under such conditions. More specifically, the analysis bellow is dedicated to evaluating the effect of the higher density of deep brines and the profile heterogeneity of the bed on drainage water quality characterized by the behavior of function $C(t)$.

17.1 A Brief Description of the Geological and Hydrological Structure of the Site, Drainage Measures and Groundwater Regime Disturbed by Mining Operations

Korshunovsky iron ore deposit of metasomatic magnetite type ranks among the largest in Eastern Siberia. Its development was accompanied by considerable drainage efforts aimed at dewatering an open pit mine (Fig. 17.1). The ore deposit is associated with a sub-vertical pipe-like structure (filled with ore minerals) that bursts surrounding rocks of sedimentary type of Cambrian and Ordovician age (Fig. 17.2). An abrupt (by more than 200 m) drop in the head in the upper aquifers has caused changes in their hydrodynamic interaction with lower aquifers: the downward water flow (under natural conditions) changed to the reverse, upward flow. This created the conditions for discharge of natural brines, contained in lower horizons, into the drainage system of the open pit mine. The discharge of saltwater extracted by the drainage system is comparable with the flow rate of the Korshunikha River, which is the main water stream in the region. Such situation causes serious environmental problems in the region. Their solution involves the construction of hydrogeological models allowing one to describe and predict the observed saltwater upconing.

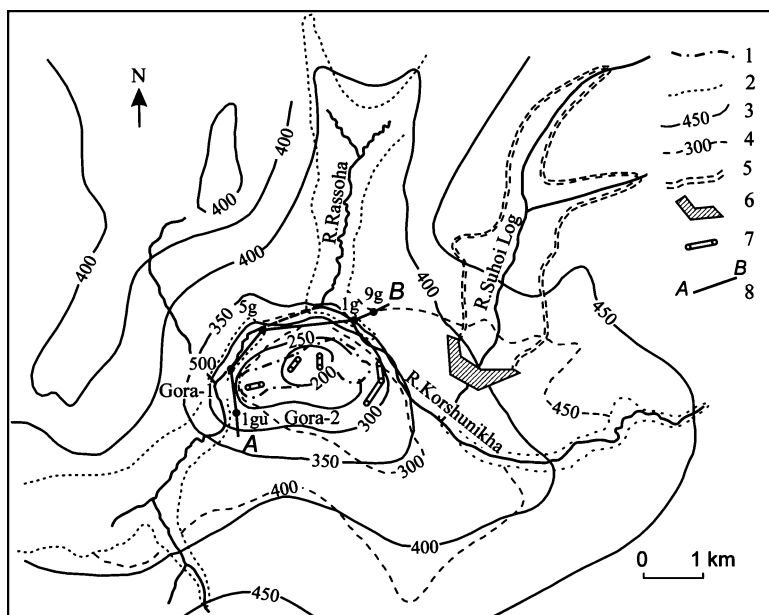


Fig. 17.1 Hydrogeological scheme of the Korshunovsky iron ore deposit. (1) The boundary of the ore body, (2) outcrop area of Verkholenskaya formation, (3) hydroisohypses (December 1994), (4) contour lines of the roof of Verkhnelenskies deposits, (5) tailing-pond outline, (6) tailing-pond dike, (7) drainage systems, (8) section line (see Fig. 17.2)

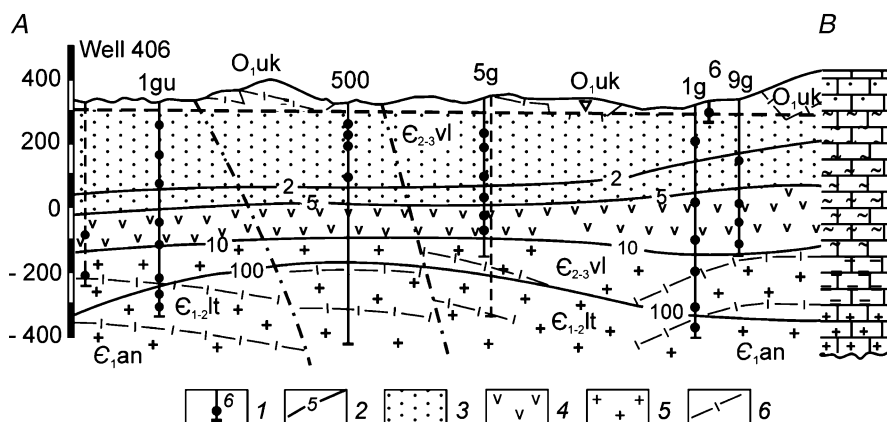


Fig. 17.2 Scheme of hydrochemical zonality of the Korshunovsky iron ore deposit. The section line passes along a profile of wells around the ore body. (1) Wells and sampling intervals, (2) salinity (TDS) contour lines, (3–5) chemical type of water (Ca-SO₄, Na-Ca-Cl-SO₄, Na-Cl, respectively), (6) boundaries of geological layers

17.1.1 Hydrogeological Units

The section of the water-bearing sediments and rocks that surround the iron ore body being developed (Fig. 17.1) and contribute to the formation of saltwater inflow to the drainage system within the open pit mine contains two major aquifers that differ in permeability and groundwater quality characteristics:

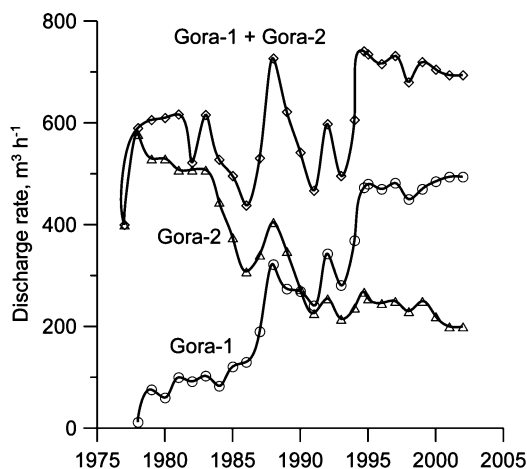
- an aquifer of the Verkholenskaya formation of Middle–Late Cambrian, confined to “speckled” sediments (alternation of limestones, marls, argillites, and sandstones with a total thickness of 550–600 m); the hydraulic conductivities of the fractured rocks are 0.01–0.5 m/day, with a mean of 0.25 m/day;
- a combined aquifer of Litvintevskaya and Angarskaya formations associated with carbonate salt-bearing rocks of Lower Cambrian and having lower permeability (the hydraulic conductivity does not exceed 0.1 m/day).

17.1.2 Drainage of the Open Pit Mine

Since 1973/1974, the problem of effective drainage of the Korshunovsky iron ore open pit mine was solved by creating well groups for local drawdown in preblasted mass of hard ores (artificial drains) concentrated in two areas in the ore deposit with conventional names “Gora-1” and “Gora-2”.

Between 1977 and 1988, the volume of water inflow to drainage systems in the Gora-1 area was gradually increasing, while the inflow to the Gora-2 drainage system (Fig. 17.3) was gradually dropping. The total water inflow remained about the

Fig. 17.3 Mean annual yield of drainage systems within the open pit mine



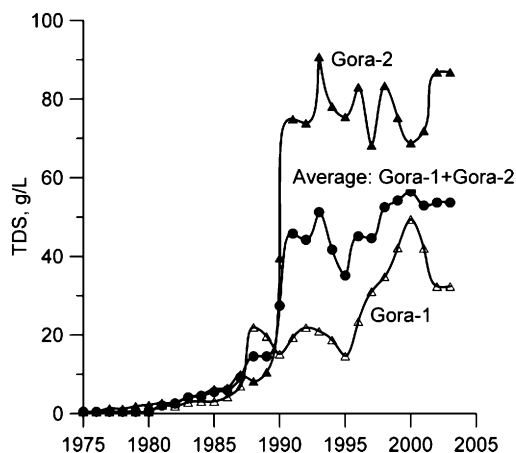
same (500–600 m³/h) both in this period and later up to the late 1990s–early 2000s. The operation of these wells ensures the drawdown of groundwater level below the floor of the open pit mine, thus allowing the ore horizons to be processed practically dry. However, the localization of water inflow induced pulling of deep salt water toward the drainage systems within the open pit mine.

17.1.3 Vertical Hydrogeochemical Stratification of the Groundwater System and Temporal Changes in Groundwater Quality

The considered groundwater flow system exhibits vertical stratification of the geochemical settings. This stratification is conditioned by (a) the geochemistry of water-bearing rock composition, (b) the history of the geological development of the region, (c) the specificity of the regional hydrodynamics. Widespread in the territory of the Korshunovsky iron ore deposit are carbonate rocks and salt-bearing formations whose composition includes rock salt and gypsum, which determine the chemistry and salinity of groundwater.

The distinguished aquifers were found to have a distinct vertical geochemical zonality (Fig. 17.2): an increase in groundwater salinity with depth is due to the greater salinity of rocks and the hampered water exchange in the bottom zones of the section. The maximal TDS (about 350 g/L) is typical of water in the Litvintsevsky and Angarsky aquifers, tapped at depths of 600–700 m (the absolute elevation of the roof is about –350 m). The boundary between the low-salinity (<3–5 g/L) and high-salinity (>100 g/L) waters is relatively contrast; the increase in concentration $C(z)$ over depth within the transitional zone is of exponential character (Mironenko and Rumynin 1999).

Fig. 17.4 Mean annual salinity values of water pumped out by different drainage systems



Not only the total concentration of components increases with depth, but also the type of groundwater changes, creating the hydrochemical zonality, which, as a rule, is clearly seen throughout the section of the water-bearing stratum (Fig. 17.2). As mentioned above, the observed natural hydrochemical zonality of groundwater proved to be extremely unfavorable in terms of the environmental consequences of the open pit mine development.

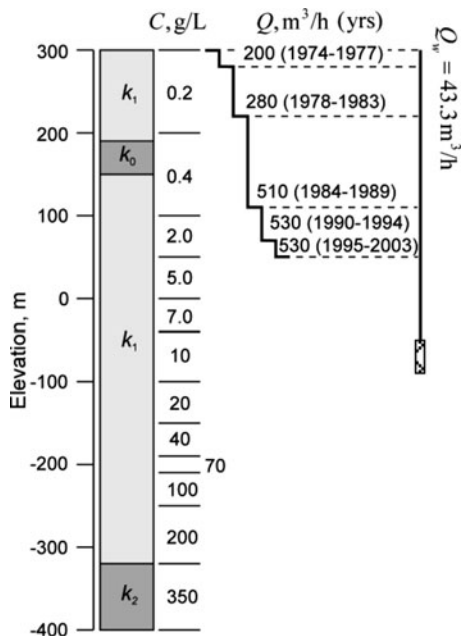
Since the moment when the system of local drawdown was created, some changes appeared in drainage water chemistry; the deepening of the open pit mine was accompanied by an increase in water salinity (Fig. 17.4). The plot of such changes was constructed based on data on mean annual values of salinity of drainage water withdrawn by different dewatering systems within the open pit mine.

The ascending motion of solutions is caused by the considerable drop in the heads (the current drawdown is more than 200m in the center of the depression cone) in the upper aquifers being drained, thus creating favorable conditions for the discharge of high-head water from the lower hydrodynamic stage. Mixing with less saline and fresh groundwater in the upper horizons, these solutions increase the total salinity of the drained water.

17.2 Analytical Assessments

It is reasonable to assume that the abrupt increase in the growth rate of water salinity (in period 1986–1988) is due to the deepening of drainage facilities below some low-permeability bed, which had long served as a screen preventing saltwater from discharging into the open pit mine (Fig. 17.5). Only small portions of salt water could penetrate through local high-permeability zones, thus increasing water salinity to 7–10 g/L. Comparing the schedule of mining operations and variations in salinity shows that such screening bed should lay near elevations of +180 ... +150m.

Fig. 17.5 A conceptual scheme for the estimation of subvertical migration of brine in the Korshunovsky iron ore deposit. $k = k(z)$ is hydraulic conductivity; $C = C(z)$ is groundwater salinity; Q is the total discharge of the drainage system (the numbers in parentheses are the time intervals during which the given discharge remained constant); “steps” on the broken line correspond to the depth of the open pit mine at the end of the appropriate time interval; the vertical line is for the test well remote from the open pit mine (Q_w is well yield)



As a very approximate interval-type estimates, we can assume that the main process of water pulling started at the moment when layers below the elevation of +150 m were uncovered (13 years after the system of local drawdown was put in operation). Now the total thickness of water-bearing beds below this elevation is $m = 550$ m (Fig. 17.5). The mean deepening of the draining contour (l) is 60 m, and its capacity is $Q = 3Q_{\text{act}}/4 = 9180 \text{ m}^3/\text{d}$ (considering that about 25% of water still enters from the upper parts of the section; $Q = Q_{\text{act}} = 12240 \text{ m}^3/\text{d}$ ($510 \text{ m}^3/\text{h}$) is the total discharge from two areas).

If we assume the groundwater flow to have cylindrical symmetry, the concentration function $C(t)$ can be calculated from (14.9). The main difficulty is the assessment of the occurrence depth of the saltwater bed in the presence of a transitional zone (Figs. 17.2 and 17.5).

In this case, we propose a procedure for constructing function $C(t)$ for a range of values of b (see Sect. 14.2.3.2), where each value of b corresponds to a specific combination of the mean concentrations C_f and C_s of the initial step-wise function ($C(z) = C_f$ when $0 < z < b$ and $C(z) = C_s$ when $b < z < m$), defined as:

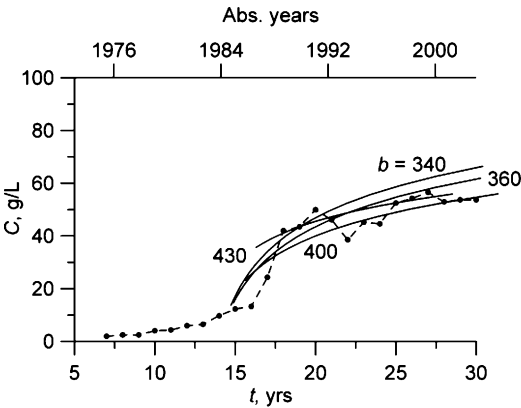
$$C_f = \frac{\int_0^b C(z) dz}{b} \text{ and } C_s = \frac{\int_b^m C(z) dz}{m - b}.$$

Calculations by these formulas, where the specified values $(m - b)$ characterize the zone $C(z) > 100 \text{ g/L}$, are given in Table 17.1.

Table 17.1 Calculated concentrations C_f and C_s at different b

A.e., m	b , m	C_f , g/L	C_s , g/L	Q/Q^*
-190	340	11.4	226	2.21
-210	360	14.6	242	1.84
-250	400	23.2	280	1.29
-280	430	35.6	300	1.08

Fig. 17.6 The results of analytical calculations of function $C(t)$ with different b , m (see Table 17.1); dots are observation data on mean water salinity, t is time since the beginning of drainage operations



The general solution has the form

$$C = (C_s - C_f)\bar{C} + C_f,$$

where $\bar{C}$ is defined by (14.9); the density gradient was calculated assuming a linear dependence $\rho(C)$ at $C_{\max} = 350$ g/L, $\rho_{\max} = 1300$ kg/m³; $k_r = k_z = 0.025$ m/d; $R = 10000$ m.

The plot in Fig. 17.6 shows that the observation data generally fall within the interval of theoretical plots of $C(t)$, though the observed values show a greater tendency toward stabilization. Such stabilization can be due, in particular, to the effect of infiltration of atmospheric precipitation, diluting deep brines, and to the limited thickness of the bed, which is not accounted for in the formula. It should be also mentioned that the analytical solution was derived for idealized conditions: an abrupt interface between fresh and salt waters, the contact between the well and the impermeable roof of the aquifer, the constant length of the water intake interval, the constant discharge rate, etc. This is the main cause of discrepancies between the actual and calculated concentrations (Fig. 17.6).

17.3 Numerical Modeling

As it was mentioned above, the modeling was aimed at testing a working hypothesis yielding a physical explanation of the nonmonotonous character of the observed salinity growth in groundwater withdrawn by drainage systems within the open pit

mine field. Also useful is the evaluation of the effect of vertical density gradient onto the salinity function. Having in mind the conceptual character of the estimates, we can restrict ourselves to formulating the problem in cylindrical coordinates.

17.3.1 Process Conceptualization and Model Design

The water withdrawal systems within two zones in the open pit mine (Gora-1 and Gora-2) were regarded as a single (generalized) interval of stratum drainage. The position of this interval within the model section was changed over time in a discrete manner in accordance with the main stages of the open pit mine development. The length of the interval approximately corresponded to the mean depth of the open pit mine for certain time intervals, associated with model stress-periods (Fig. 17.5). Essentially, considering the cylindrical symmetry, we simulated water intake from a partially penetrating well with a considerable radius, equal to the mean radius of the open pit, $r_{op} = 200$ m; the radius of influence, $R = 10,000$ m.

The original zonality of groundwater in terms of salinity is very heterogeneous (Fig. 17.5), causing a progressive growth in water density over depth. The variations in appropriate characteristics (the salinity, $C(z)$, and density $\rho_s(z)$) were approximated by a step-wise function including 12 fragments or “steps.” The maximal density (at the 12th fragment, where $C = 350$ g/L) was $1,300$ kg/m³.

The permeability (hydraulic conductivity) k_1 of the Verkholsenskaya formation in the elevation interval between $+300$ m (the roof) to -320 m (the floor), estimated from pumping tests and the operation drawdown is 0.25 m/day. However, a seam with a relatively low permeability $k_0 \ll k_1$ can be assumed to exist in the section of Verkholsensk rocks in the depth interval from $+190$ to $+150$ m. It is the uncovering of this layer by the open pit that could cause an abrupt intensification of the ascending migration of deep brines and, accordingly, to an abrupt increase in the salinity of the extracted water. The underlying rocks of the Litvintsevskaya formation have the hydraulic conductivity of $k_2 = 0.1$ m/d.

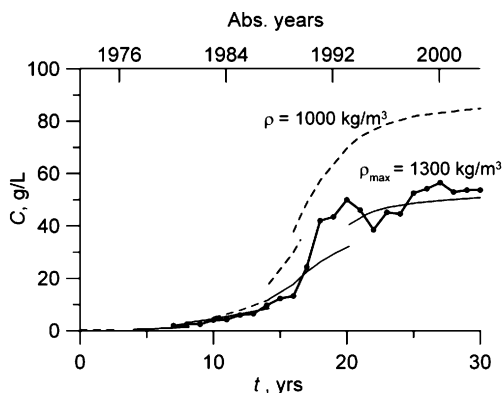
The porosity of the entire stratum is estimated at $\phi = 0.07$ based on the experience of previous studies (Mironenko and Rumynin 1999). The parameter ϕ indirectly (effectively) accounts for the block (between fractures) storage capacity of the permeable medium.

The profile structure of the model was represented by 70 model layers, each 10 m in thickness. In the planar view, the size of the cylindrical blocks changed according to a logarithmic law from 200 m (the first block – the open pit) to 513 m (the 30th block – the boundary). The problem was solved in the confined-flow formulation.

17.3.2 Modeling Results

Modeling consisted in the choice of the permeability k_0 of the low-permeability layer. The plot of variations in the mean salinity $C(t)$ of water withdrawn by the

Fig. 17.7 Comparison of model calculations and observation data on mean salinity (dots on the curve). The full curve is for $\rho = \rho(z)$, the dashed line is for $\rho = \rho_f = \text{const}$



drainage system (Fig. 17.4) was used as an efficiency function. An acceptable agreement between the model results and the actual curve $C(t)$ was attained at $k_0 = 0.005 \text{ m/d}$ (Fig. 17.7). As can be seen, the calculated curve shows a much faster increase in water salinity in period 1986–1988 when the roof of the deposits underlying the low-permeability bed was uncovered.

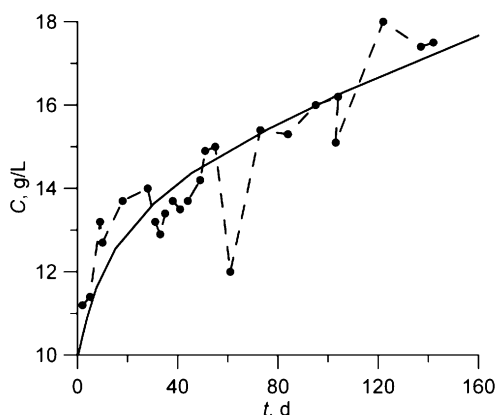
The plot also gives the results of calculations made with water density assumed constant: $\rho = \rho_f = 1000 \text{ kg/m}^3$. In this case, the model data are seen to largely overestimate the recorded values.

17.3.3 Experimental Verification

The validity of the assumptions used in model schematization and the correctness of the chosen parameter values were verified using data of modeling a long (5-month) pumping out of a well located far from the open pit (Fig. 17.5); the well had a screen within depth interval of $-350 \text{ m} \dots -390 \text{ m}$; the pumping rate was $1,040 \text{ m}^3/\text{day}$; during the pumping, water salinity increased from about 10.5 to 17.5 g/L . The well was simulated by four blocks (each 10 m in size). The concentration was averaged over two bottom blocks. As seen from Fig. 17.8, the model plot adequately describes the trends in water salinity recorded during the test.

Overall, the data of observations of dissolved-salt redistribution in the aquifer along with records of the dynamics of variations in head field, both during pumping tests and the operation of hydrogeological objects, open up new possibilities in calibration of groundwater flow and solute migration models, as is demonstratively shown by the results of modeling a process of subvertical groundwater migration (van Meir and Lebbe 2002). The efficiency of such combination can be improved by the involvement of data of isotopic hydrogeological monitoring.

Fig. 17.8 Model interpretation of the results of a long-time pumping test. Dots show salinity measurements in the pumped-out water



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Chapter 18

Light Wastewater Injection into a Deep Geological Formation Containing Brine (“Volzhsky Orgsintez” Deep-Well Disposal Site, Central Russia Region)

Deep-well disposal (injection) of hazardous chemical waste (DWWD) has been widely practiced around the world for many years (Tsang 1996; Clark et al. 2005; Tsang et al. 2008). It was proved that in many cases the DWWD technology is the only disposal option that effectively removes waste from the biosphere.

This method of waste isolation can be also attractive due to its cost-effectiveness. Injection of wastewater into a geological formation can activate a great number of complex chemical reactions and material or energy transport phenomena. Some of them will be analyzed later, in Chap. 23. This chapter will focus mostly on the identification of phenomena associated with the regional hydrogeology of deep groundwater systems that can have a dramatic effect on the accuracy of hydrogeological interpretation of field data and groundwater flow and transport modeling, and consequently on reliability of long-term prediction of waste migration, specifically when the formation water is of a higher density than the injected wastewater. One goal of this study is to identify the features of subsurface hydrodynamics of a sloping, heterogeneous, spatially bounded aquifer, which is a host reservoir for wastewater. This study also addresses the related issue in waste repository predictive modeling from a viewpoint of flow model calibration under heterogeneous initial salinity conditions occurring in a sloping aquifer.

The study is based on materials of geological-structural analysis, hydrogeological tests, and monitoring studies carried out at a DWWD site connected with the Volga Organic Synthesis Plant (“Volzhsky Orgsintez”) located in the central part of Russian Federation for approximately 20 years starting from 1992.

18.1 Hydrogeological Characteristics and Setting of the Geological Environment

18.1.1 Available Field Data

A general scheme of the area with the layout of injection (working) and observation wells is given in Fig. 18.1. The distances from the center of the cluster of recharge

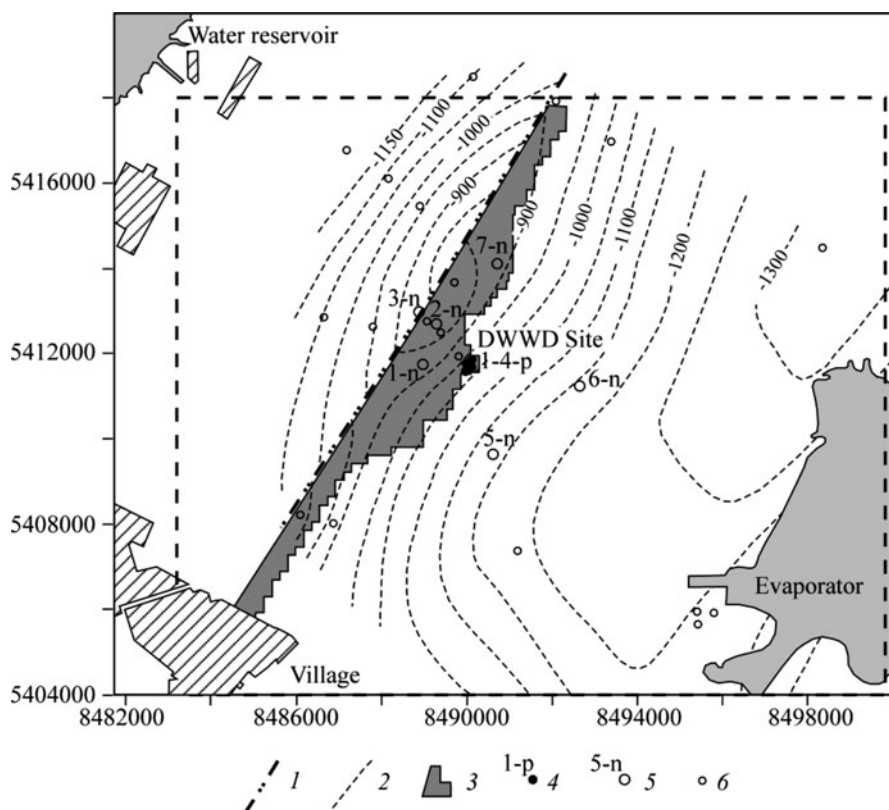


Fig. 18.1 A regional structural scheme of the Lower Bayeux aquifer. (1) Tectonic fault (western fault); (2) bed roof topography (absolute elevation, m); (3) higher permeability sediments (the zone is identified by modeling data); (4) injection well; (5) observation well; (6) exploration or inspection well. The dashed line rectangle is the model domain. Geographic coordinate system, m

(injection) wells to the nearest and the furthest observation wells, 1-n and 6-n, are about 1,030 and 2,700 m, respectively (Fig. 18.2).

From the viewpoint of structural geology, the DWWD site is located within an anticlinal, which is commonly referred to as the Eastern Poromenky trough. The anticlinal is a part of a sedimentary basin including the so-called Lower Bayeux aquifer (Fig. 18.1; see also Fig. 18.4). The aquifer consists of sands with a relatively high permeability, which are confined vertically by impermeable clay strata. The mean aquifer thickness is 25 m. According to geophysical data, domains with different clay content were identified, demonstrating variations in the effective thickness of the aquifer. Aquifer material porosity, ϕ , varies from 18% to 25%.

Recharge well cluster (1-p, 2-p, 3-p, and 4-p) is shifted toward the uplifted part of the folded strata. The positions of the four observation wells, 1-n, 2-n, 3-n, and 7-n are also confined to the dome of the structure, while two observation wells, 5-n and 6-n, are located on its wings. Thus, well screens tap the aquifer at different

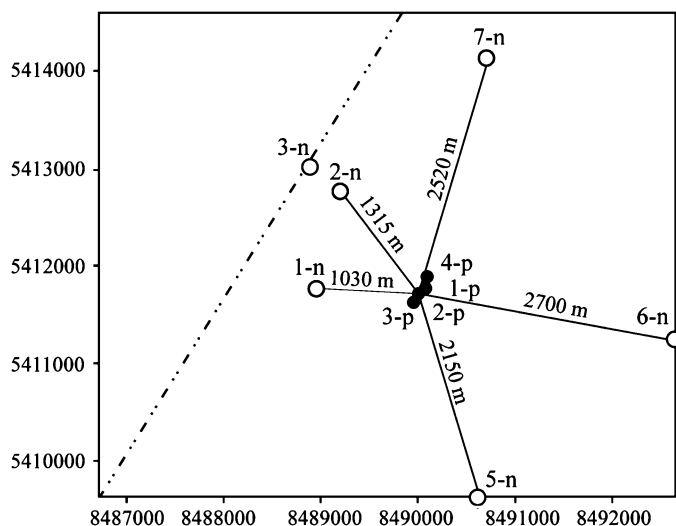


Fig. 18.2 Layout of injection (full circles) and observation (hollow circle) wells at the DWWD site. The dash-double-dot line is the western fault

absolute elevations (from -850 to $-1,150$ m), the fact that, as shown below, is of principal significance in calculating the pressure head in the presence of abruptly heterogeneous hydrochemical zonality.

The main tectonic faults are associated with the core of the anticlinal structure. Higher aquifer material permeability values can be expected here. At the same time, faults can work as screens. Indeed, the operation experience of the waste disposal system demonstrates that the propagation of hydrodynamic perturbation in the western direction is limited by the line of the regional fault shown in Figs. 18.1 and 18.3. The screening properties of this geological formation are confirmed by a very weak hydrodynamic response of the observation well 3-n to wastewater injection into the aquifer.

Groundwater samples were taken from piezometers with screens installed at different depths. It was established that the salinity of groundwater in the Lower Bayeux aquifer varies drastically with total dissolved solids (TDS) between 80 – 100 and 150 – 200 g/L (Figs. 18.3 and 18.4). At the same time, hydraulic (piezometric) head measurements in piezometers (before the operation of the waste disposal system) have shown that, in addition to the above-mentioned TDS variations, the aquifer features a considerable slope in the hydraulic head surface, on the average from $+7$ to -55 m within a distance as short as several kilometers (Figs. 18.3 and 18.4). It is clear that the gradients of hydraulic heads as large as these can only be caused by spatial variations in the density of the formation liquid.

On the other hand, density variations in groundwater can create a buoyancy driving force that can significantly alter the flow magnitude and direction inferred from maps of piezometric surface (Bachu and Michael 2002). Therefore, further

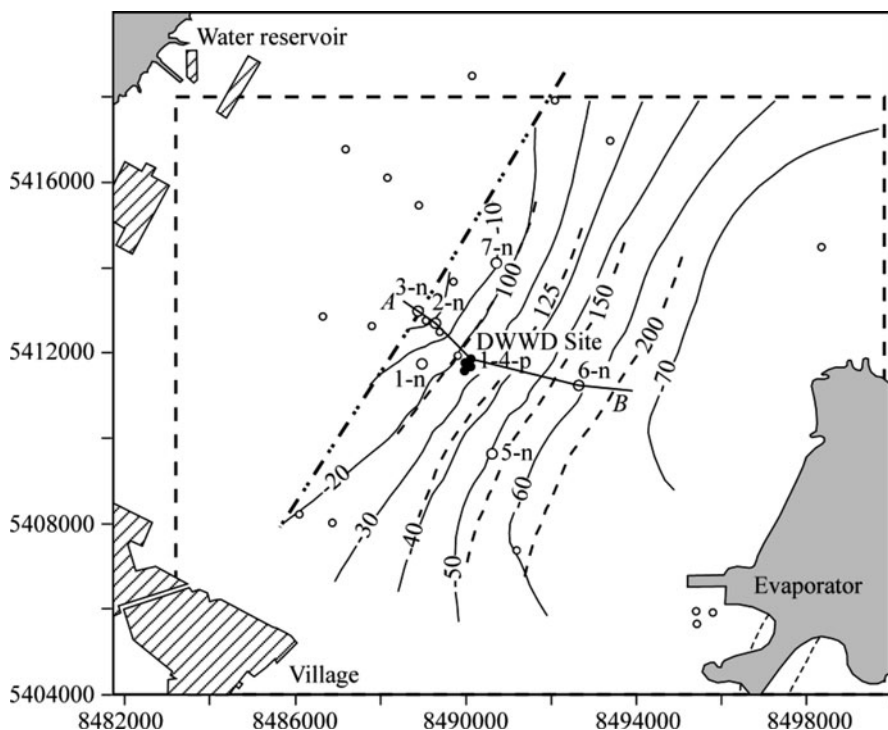


Fig. 18.3 A map of initial hydraulic head, m (*solid lines*) and salinity (TDS), g/L (*dashed lines*) of groundwater hosted by the Lower Bayeux aquifer. A–B is the line of schematic hydrogeological section (Fig. 18.4). Other denotations see in Fig. 18.1

investigation of regional flow of variable density in structurally sloping aquifers and solution of local wastewater migration problems in terms of hydraulic head can lead to errors (Post et al. 2007). A fluid pressure-based formulation is obviously a more preferable option in modeling the variable-density problems related to the DWWD site under consideration.

The waste disposal site has been in operation since 1992. The volumes of annual injection of industrial wastes vary from 200 to 870 thousand m^3 (Fig. 18.5). About 110 thousand m^3 were injected in 2007. The volume of wastes buried in the Lower Bayeux aquifer by 2008 is about 9.5 million m^3 .

Liquid wastes are produced in the process of gasoline additives and nutritive methionine (an amino acid) production and a preparation to speed the vulcanization of rubber. The wastes contain a series of chemicals of organic origin (aniline, phenols, toluene, benzol, naphthalene, spirits, oil products, etc.). The TDS of the pumped wastes varies between 5 and 10 g/L, which is far below the TDS of the formation water (90–180 g/L). Therefore, there is a significant difference in the physical properties (density and viscosity) of the formation and industrial waters. Again, these waters belong to different hydrochemical types. In particular, useful markers,

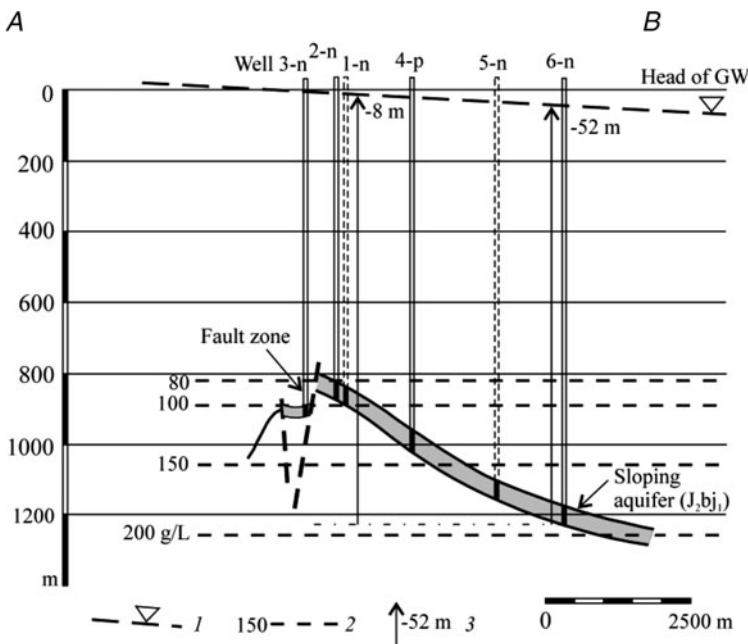


Fig. 18.4 A schematic hydrogeological profile of the DWWD site showing the influence of hydrochemical stratification on apparent groundwater head distribution. (1) Piezometric (hydraulic head) surface, (2) line of constant salinity (TDS), (3) calculated hydraulic head

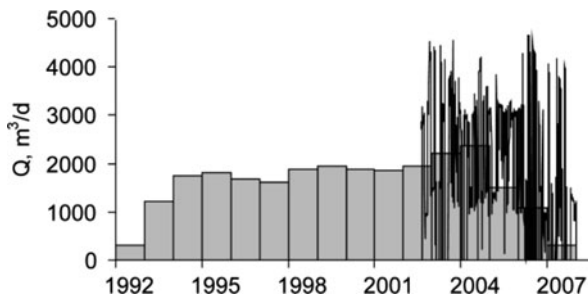


Fig. 18.5 The volumetric flow rate of liquid waste injection into aquifer, m³/day. The broken line shows the actual (daily based) measurements, the rectangles show the recharge rate averaged over a year

demonstrating the propagation of the mixing zone of formation and waste waters are chloride and sulfate ions: industrial waters are low in Cl^- (no more than 50–250 mg/L), whereas the initial concentration of these ions in the formation water near the operation wells reaches 35,000–55,000 g/L. Conversely, the concentration of SO_4^{2-} in the wastewater is greater (up to 4 g/L) than its concentration in groundwater (1.5–2.5 g/L).

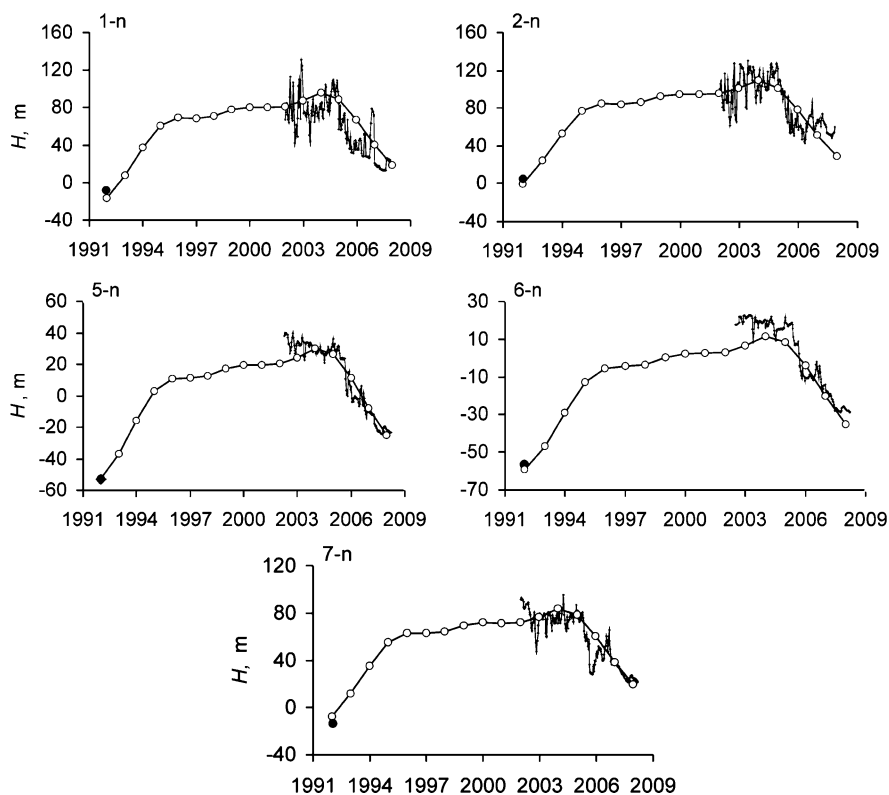


Fig. 18.6 Hydraulic head (true altitude, m) measured in piezometers 1-n, 2-n, 5-n, 6-n, and 7-n. Thin broken lines are actual data, smooth lines and hollow circles show the model solution. Full circles show head values before injection

Detailed monitoring of piezometric head using observation well network has been carried out since 2002. The wells were equipped with manometers, allowing measurements to be made when water head in the wells rose above the land surface. The values of all measurements were converted into the absolute elevations of the piezometric surface (Fig. 18.6). The pressure in injection wells was measured in a similar way. A characteristic feature of the behavior of the head curves is a delayed response of the hydrodynamic system to shutdown of operation wells: the heads are found to drop slowly, suggesting a considerable effect of the storage parameters.

Standard aquifer pumping and slug tests were carried out at the site in different periods. The studies were mostly focused on the aquifer zone adjacent to injection wells. The mean transmissivity is $60 \text{ m}^2/\text{day}$; with the effective thickness of the bed of 30 m, this value corresponds to the hydraulic conductivity, k , of 2 m/day. The hydraulic diffusivity is about $7 \cdot 10^5 \text{ m}^2/\text{day}$. However, the need to solve problems involving the flow of liquids with variable density and viscosity, makes it more correct to use the aquifer permeability. Indeed, it can be readily shown that changes

in water density (from 1.04 to 1.13 g/cm³) and viscosity (from 1 to 2 cP) within the zone of influence of the hydrodynamic perturbation caused by the operation of the injection system results in a change in the hydraulic conductivity by a factor of about 2. Therefore, hereafter we will use the aquifer permeability, K .

18.1.2 Conceptualization of the Hydrogeological Setting and Model Description

A key point in the schematization of initial conditions is the specification of heterogeneous spatial distribution of fluid density, controlled by variations of total dissolved solids (TDS) in groundwater. A conceptual scheme in Fig. 18.4 explains that the observed variations in TDS in the planar view are a consequence of the profile hydrochemical zonality in a sloping aquifer, represented by the eastern wing of an anticlinal structure. Under this hydrogeological setting, the piezometers with screens penetrating the sloping bed at different depths show potentiometric surface which seems to have unrealistically high hydraulic head gradients. This phenomenon determines the specifics of the hydrodynamic response of the groundwater system to waste disposal operations that shall be taken into account in numerical modeling (Sects. 18.2, 18.3).

The hydrodynamic boundaries of the model and their physico-mathematical representation in the numerical scheme were chosen based on the analysis of the general geological-hydrogeological situation. The external boundaries of the model are the fault zone, represented by an impermeable (second-type) boundary; elements of the structure of hydrodynamic grid of groundwater flow, equipotential lines of the Lower Bayeux aquifer, which were associated with first-type boundaries ($H = \text{const}$), at a sufficient distance from the industrial-waste injection site. Inside the model domain, the recharge wells are modeled as source terms associated with model cells. Each well recharging the aquifer had its own schedule, $Q_w = Q_w(t)$.

When constructing the matrix of zones reflecting the heterogeneity of permeability, we proceeded from the specific features of the geological structure of the aquifer system. First variants of model calculations assumed a simplified homogeneous structure of the horizon: the permeability was specified in accordance with the results of aquifer pumping and slug tests performed at a local site adjusting to the recharge well cluster. An alternative is a multi-zone (heterogeneous) flow model, which takes into account a relationship between variations of flow parameters and the geological structure of the considered site (Sect. 18.2).

The modeled area is 16.6 km by 14 km in size and contains the entire study area. Such model scale allows us to eliminate the effect of planar boundaries on the flow gradient during long-term injection of industrial wastes into wells.

To provide a detail description of variations in the elevations of the roof and foot of geological beds on an orthogonal grid, the examined domain was represented by 100 model layers. In the horizontal plane the model domain was discretized in a

uniform 2-D grid of 50×50 m near the recharge wells and 200×200 m at a distance from them. The number of model cells is 116 in the sublatitudinal direction, x , and 103 in the submeridional direction, y . The major portion of the model domain, which is represented by inactive model cells, lying beyond the first-type and second-type boundaries was excluded from the calculation procedure.

The initial salinity distribution was specified in a three-dimensional space with allowance made for the hypsometric position of the bed. Data on the initial salinity, pressure in the bed, maximal density, liquid temperature, and other parameters were used to calculate the liquid density in each model cell at a series of moments with the help of TOUGH2 numerical simulator.

The model was calibrated against a piezohypse map, which provides reliable information about hydraulic-head distribution, as well as data on the time trends in variations of marking components in observation wells.

18.2 The Concept and Technique of Numerical Analysis

The investigation of groundwater flow and liquid-waste transport was carried out using a numerical simulator TOUGH2 (Sect. 14.1). Numerical analysis was primarily concerned with the following two problems. The first was flow model calibration aimed to estimate flow parameters and entire system geometry, and the second was the prediction of the wastewater–formation water (brine) interface movement and configuration.

The strategy for calibration of the groundwater flow model was to use both steady-state hydraulic head data and transient hydraulic head data. The steady state calibration was used to confirm whether the observed hydraulic head potentiometric surface is equilibrated by spatial variation of fluid density in the sloping aquifer and model geometry. Model calibration at this stage was used to test the appropriateness of simulated boundary conditions and to obtain approximate transmissivity.

The transient calibration of the groundwater flow model was based on monitoring data obtained between January 1992 and the end of 2007 when the aquifer was intensively recharged by means of waste injection. Such calibration was done by matching the time variations in the simulated and measured hydraulic head distributions (Fig. 18.6). The parameters varied during the calibration process include the hydraulic conductivity and specific yield. After each change in one of these parameters, the simulation was run and the simulated groundwater levels were compared with the observed ones.

In both approaches, steady-state and transient, model calibration was an iterative process where the model parameters are altered until the model results adequately match the field observations.

Model calibration took into account the observed trends in groundwater quality variations in the observation wells. Also, aquifer tests' results were used to improve the accuracy of the inverse flow problem solution.

The numerical solution of steady state problem confirmed the conclusion that a decrease in the absolute elevations and, hence, an increase in the salinity and density of formation water cause a drop in the hydraulic head (calculated using model pressure distribution): the head in the lowest areas in the bed is -80 m, while it reaches the elevation of 0 m near the fault, a fact that is in agreement with observational data.

The functioning of a system of injection wells yields a seemingly illogical head distribution (Fig. 18.6): the increase in head in individual observation wells located closer to the center of the operation well group yields lesser rise in water level in them than in more distant wells, so first versions of calculation, assuming a homogeneous bed, yielded unacceptable results.

Therefore, further solution of the inverse problem required the identification of two aquifer zones with different permeability, followed by a directed choice of permeability values for each zone. The spatial position of the first zone was associated with a higher permeability block within the dome of anticlinal structure. This zone is oriented along the fault strike (see Fig. 18.1). The zone was studied by aquifer tests, which yielded mean values of transmissivity of $60 \text{ m}^2/\text{day}$ and hydraulic diffusivity of $7 \cdot 10^5 \text{ m}^2/\text{day}$. These values remained invariable during model calibration. The second zone of hydraulic heterogeneity can be associated with the zone of rock occurrence in the eastern flank of the anticlinal structure. This zone, remote from the tectonically active area, should be expected to feature lower permeability. The appropriate value was chosen during the solution of inverse problem. Thus, model calibration involved the adjustment of two parameters: the permeability of the zone with relatively low permeability and aquifer compressibility, which is a component of expression for hydraulic diffusivity.

Multivariant model calculations yielded $6 \cdot 10^{-13} \text{ m}^2$ for the permeability of the groundwater reservoir in the eastern block, so the transmissivity due to variations in liquid properties and sediment thickness was estimated as varying from 15 to $25 \text{ m}^2/\text{day}$. The coefficient of compressibility was found to be $2 \cdot 44 \cdot 10^{-9} \text{ Pa}^{-1}$, yielding the hydraulic diffusivity of about $5 \cdot 10^4 \text{ m}^2/\text{day}$ (this expression appears to reflect compressibility of clay sediments in the stratum overlaying the Lower Bayeux aquifer). The accuracy of the problem solution can be judged from the plots in Fig. 18.6, demonstrating time variations in groundwater head in observation wells.

Visualization of model results shows that the injection has resulted in the formation of a cone (Fig. 18.7), whose asymmetric shape is determined by the existence of a contact between rocks with different permeability, as well as by the screening effect of the western tectonic fault located near the injection-well group. The errors in the reproduction of heads within the model domain vary from 5% to 10% , meeting the requirements of detail and reliability of further analysis. The obtained matrix was directly used in constructing mass transfer model.

Interestingly, the nonsteady model was found to be sensitive to the choice of aquifer compressibility. The value of this parameter allows one to adequately simulate the observed effect of “hanging” of the cone, taking place in the case of slowed dynamics of head drop in wells after a shutdown of the injection system.

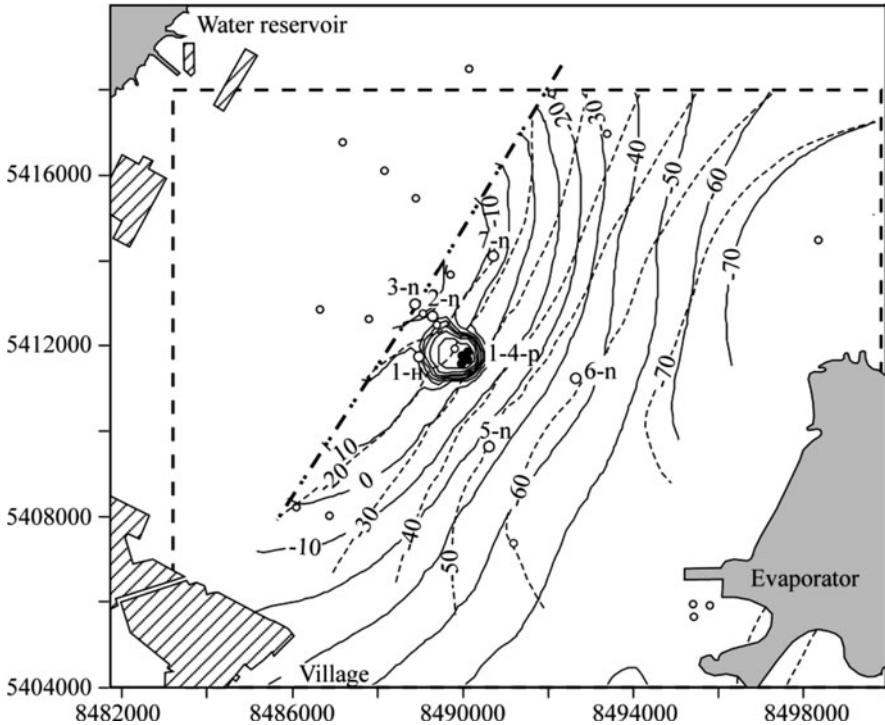


Fig. 18.7 A map of equivalent hydraulic head (m, *solid lines*) as a result of modeling for 2007. The *dashed lines* show the initial hydraulic head distribution; other items of the legend see in Fig. 18.1

18.3 Numerical Solution of a Groundwater Transport Problem

The calibration of groundwater flow model using hydraulic head distribution allowed us to use output data of the TOUGH2 solute transport subroutine for describing subsurface migration of the low-salinity (total dissolved solids, TDS) wastewater injected into a saltwater aquifer. A solution of the migration problem is presented (Figs. 18.8 and 18.10) in contour lines of dimensionless TDS,

$$\bar{C} = (C^0 - C) / (C^0 - C_0),$$

where C^0 is the initial TDS of the formation water, C_0 is the TDS of the injected wastewater, 5–10 g/L.

Data of modeling as of 2007 (reference time, Fig. 18.8a) show, in particular, that the wastewater front has reached the observation well 1-n, which is in agreement with data of its hydrochemical monitoring. The relative amount of wastewater in water samples taken from this observation well ranges between 15% and 30% (these values were calculated using chloride ion content). The numerical simulation

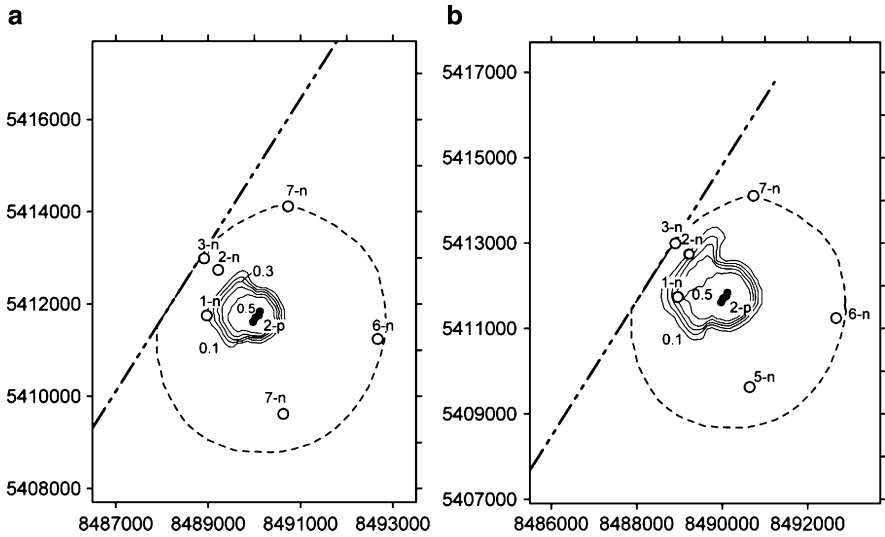
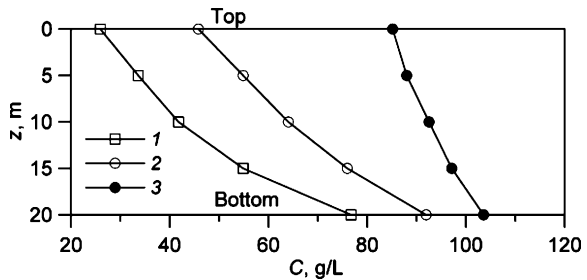


Fig. 18.8 Variations of the relative salinity of formation water for (a) 2007 and (b) 2021. The dashed line is the boundary of the sanitary-protection zone; other legend items see in Fig. 18.1

Fig. 18.9 Salinity variations over depth in different points of the aquifer (2004). The distance from well 2-p (m): (1) 400 (to E), (2) 450 (to E), (3) 460 (to SE)



yielded the same range with the porosity specified at 25%, which is in reasonably good agreement with field data analysis of the Lower Bayeux aquifer material.

Analysis of salt distributions in the cross section demonstrates a clear tendency toward the predominant spreading of light wastes near the roof of the bed (Fig. 18.9).

The character of wastewater spreading for the prediction time (2021) is illustrated by Fig. 18.8b. The total discharge rate was 800 thousand m^3/year . It was distributed in proportion between three working wells. The presented maps reflect the decrease in water salinity (in relative units) with respect to the initial (background) state – before the start of injection system operation. We see a heterogeneous picture (in planar view), which is related with the reflecting effect of the impermeable fault and the existence of a higher permeability zone east of it. The main conclusion is that, during the model period (up to 2021), the waste will not migrate in the Lower Bayeux aquifer beyond the bounds of the sanitary-protection zone.

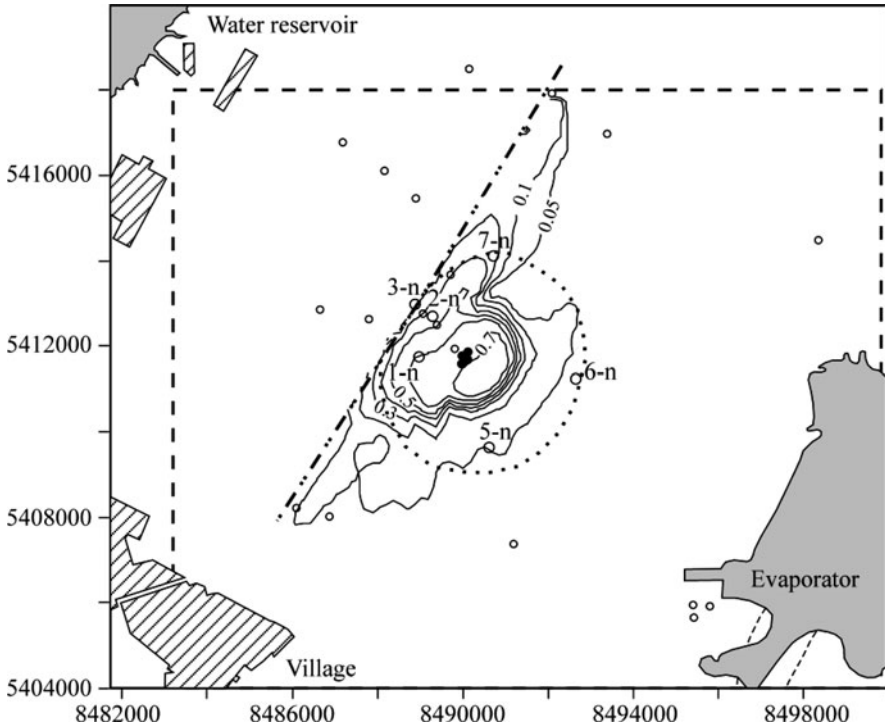


Fig. 18.10 The position of the plume (relative changes in the salinity) for 2072 (80 years after the start of disposal site operation)

The last model calculation (Fig. 18.10) was carried out to evaluate the time required for the plume to approach the boundary of the sanitary-protection zone. As can be seen, the polluted-water front cannot be expected to reach this boundary before 2072. The only exception is the northeastern zone along the fault, composed of sediments with higher permeability and filled with groundwater with lesser density.

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Part VII

Physicochemical Description and Mathematical Formulation of Sorption Processes

Apart from dissolution/precipitation reactions, most physicochemical interactions accompanying subsurface solute transport are generally referred to as adsorption or sorption reactions. These involve the loss of chemical components from an aqueous to a contiguous solid/mineral phase. In many cases, sorption is the most significant chemical process affecting the mobility of contaminants in the subsurface. Adsorption reactions are discussed primarily in terms of intermolecular interactions between a solute and solid phases, and can be generally categorized as either physical adsorption, chemisorption, or electrostatic adsorption ([Sparks 2003](#); [Encyclopedia of Surface and Colloid Science et al. 2006](#)).

Weak molecular forces, such as Van der Waals forces, provide the driving force for physical adsorption, while chemical reactions form chemical bonds between the compound and the surface of the solid in chemisorption. Electrostatic adsorption involves the adsorption of ions through Coulombic forces, and is normally referred to as ion exchange. Interphase interactions can be described also as a series of surface complexation reactions between dissolved ions and mineral surface, as well as specific adsorption. Specific adsorption is an interaction stronger than the electrostatic interaction ascribed to exchange reactions. The nature of the forces involved in the specific adsorption of ions at the mineral-matrix/pore-solution interface is not always fairly well identified.

The process in which chemicals become associated with solid phases is often referred to as *sorption*, especially when one is not sure whether one is dealing with adsorption (attraction and bonding onto a two-dimensional surface) or absorption in which the solute is taken up into a three-dimensional matrix ([Cantrell et al. 2002](#); [Sparks 2003](#)). In our analysis we do not emphasize the difference between sorption and adsorption terms. In majority of cases they are believed to be synonymous.

The most common models consider sorption as instantaneous and reversible processes. However, these assumptions are not always valid for natural soils and aquifer materials: kinetic effects are sometimes observed and significant differences may occur between sorption and desorption processes, resulting in irreversible reactions or very slow desorption kinetics.

The sorption process is particularly important for the transport of contaminants with mobile aqueous phase in the subsurface environment. Sorption of dissolved contaminants onto the soil and rock matrix results in slower transport (retardation) of contaminants relative to water velocity and a decrease in solute concentration. On the other hand, adsorption onto mobile colloids present in groundwater typically enhances the transport of contaminants traditionally considered as strongly sorbing species having low potential for mobility, e.g., actinides. The degree to which colloids enhance the transport depends on the adsorption–desorption kinetics (see Part IX).

Chapter 19

Conceptual Models for Sorption Under Batch Conditions

19.1 Sorption Equilibrium

In equilibrium, the amount of a dissolved component, N , adsorbed on soil or aquifer material and the concentration of this component in the liquid phase, C , at a given temperature and pressure satisfy a unique relationship $N = f(C)$, referred to as the (single-component) *sorption isotherm (model)*. Empirical coefficients of the sorption isotherms are determined by the energy of the different adsorption sites and the nature of liquid/solid interactions (Venitcianov and Rubinshtein 1983). Under certain conditions, sorption processes are only partially reversible, so the desorption parameters may differ, in one direction or another, from the sorption parameters. This is a manifestation of sorption hysteresis (Sect. 19.1.3).

Despite the fact that sorption reactions can be described by various isotherms/models, the ability of these models to predict *multicomponent system* behavior is limited. Most common are sorption thermodynamic *multicomponent models* describing the competitive equilibrium adsorption from real solutions containing *major (principal)* ions and *trace components* (e.g. dissolved ions of heavy metals and radionuclides). However, the application of such models requires a vast collection of thermodynamic and experimental data, which are not always available. Moreover, multicomponent approach is too mathematically complicated to be used in practice. As a result, until now the most widely applicable models used to predict sorption in hydrogeological systems remain single-component isotherm models (see also some comments in Sect. 20.1.1.2).

19.1.1 Principal Sorption Isotherms

Sorption mechanism is described by a number of empirical models $N = f(C)$. In hydrogeology, linear, Henry, and two nonlinear, Freundlich and Langmuir, single-component isotherms are the most frequently used isotherms for quantifying sorption interactions.

The simplest, *one-parameter*, expression of equilibrium sorption is the linear isotherm. There are two analytical representations for the linear model:

- for porous type of sediments

$$N(C) = K_d \rho_b C, \quad (19.1)$$

- for fractured rocks

$$N(C) = K_a S_b C; \quad (19.1a)$$

here K_d and K_a are the *sorption equilibrium distribution (partition) coefficients* (their measurement units are $[L^3 M^{-1}]$ and $[L]$, usually cm^3/g and cm , respectively); ρ_b is the dry bulk density of sediment $[ML^{-3}]$; S_b is the specific surface $[L^{-1}]$; specific surface area is defined as the ratio of the fracture surface area to the volume of mobile water in the fracture. K_d and K_a values can be determined in the laboratory by performing batch equilibrium tests or column studies, and in field tracer experiments.

The distribution coefficient K_a describes the increase in solute amount on the surface of blocks (g/cm^2) with an increase in its concentration in solution (g/cm^3). Actually, the constant K_a partially reflects the sorption within clay and hydroxide coating – hard-rock weathering products, covering fracture walls (Vandergraaf Abry 1982; Kamineni et al. 1983; Vandergraaf et al. 1984; Ticknor et al. 1989; Transport and mass-exchange processes in sand and gravel aquifers 1990).

Linear equations (19.1) and (19.1a) are assumed to hold at low filling degree of adsorption centers existing on the mineral surface. With increasing filling degree, the effect of interaction between adsorbed ions (molecules) increases, resulting in this surface becoming less acceptable for components in solution: the process shifts into nonlinear domain. A manifestation of the nonlinearity of sorption process is the drop in the calculation factor K_d with increasing concentration of the substance in solution.

Freundlich and Langmuir sorption isotherms are most widely used for describing nonlinear dependences $N(C)$. Each isotherm has *two parameters*. The wide use of these isotherms is attributed, first, to their ability to describe practically any experimental data and, second, to their relatively simple form and the small number of parameters involved.

Freundlich isotherm,

$$N(C) = K_F C^n, \quad (19.2)$$

is often used to describe the sorption of radionuclides, heavy metals, and pesticides; here K_F $[M^{1-n} L^{3(n-1)}]$ and n $[-]$ are empirical, *linear and exponential*, coefficients, respectively. A characteristic feature of the nonlinear Freundlich isotherm (with $n < 1$) is that the strength of binding decreases with concentration.

Within considerable concentration variation ranges, a general approach is the nonlinear *Langmuir isotherm*,

$$N(C) = \frac{N_v K_L C}{1 + K_L C}, \quad (19.3)$$

where N_v is the total sorption capacity of the aquifer's solid phase [ML^{-3}]; K_L is a constant characterizing the degree of affinity of the adsorbent and adsorbate (bond energy constant) [L^3M^{-1}].

The Langmuir isotherm can be derived using first-order kinetic theory or thermodynamic base (Tóth 2002), while the Freundlich isotherm is purely empirical. The Langmuir isotherm has an asymptotic saturation limit N_v , while the Freundlich isotherm has no such limit, hence it is unbounded. Both isotherms have an infinite slope $dN/dC \rightarrow \infty$ with $C \rightarrow 0$. Since the differential dN/dC can be used as an element for the construction of transport models (see below), such feature of the nonlinear isotherms can be considered as their drawback.

Therefore, some researchers prefer the *three-parameter Tóth isotherm* (Tóth 1971, 2002)

$$N(C) = \frac{N_v K'_L C}{[1 + (K'_L C)^{\beta_T}]^{1/\beta_T}}, \quad (19.4)$$

which has “desirable” asymptotic properties at high and low concentrations; here N_v is the maximum sorption capacity; β_T is the Tóth model exponent; with $\beta_T = 1$ this isotherm reduces to the Langmuir sorption isotherm, Eq. 19.3; K'_L is the Tóth model coefficient, characterizing the affinity between the adsorbate and adsorbent [L^3M^{-1}]. Isotherm (19.4), derived from potential theory, has proven useful in describing sorption in heterogeneous systems.

Nonpolar organic compounds, because of their hydrophobic behavior, are adsorbed mostly by organic matter contained in the geological sediments, soil, and aquifer materials. Therefore, the organic matter content is the factor most directly related to the sorption of organic contaminants by subsurface material. K_d shows a linear dependence on the concentration in sediment of organic carbon f_{OC} , which is the major component of soil organic matter (Reactions and movement of organic chemicals in soils 1989; EPA 1996; Sharer et al. 2003; Tinsley 2004; Riley et al. 2006):

$$K_d = f_{OC} K_{OC}; \quad (19.5)$$

here f_{OC} is the mass fraction of soil organic carbon content [MM^{-1}]; K_{OC} is the soil organic carbon-water partitioning coefficient, that is, the ratio of the mass of a contaminant that is adsorbed in the soil per unit mass of organic carbon in the soil [L^3M^{-1}]; it is the “distribution coefficient” normalized to total organic carbon content.

The values of f_{OC} vary within a wide range – from a few hundredths to a few percent. Therefore, variations in factor K_d for different substances can also be considerable. Analysis of experimental data shows (Hoffman 1995; EPA 1996) that, for halogen hydrocarbons, the values of f_{OC} exceeding 0.1% are significant from the viewpoint of the effect of sorption process on the transport of organic substances by groundwater. Several correlations are available for organic chemicals that relate the distribution coefficient, K_{OC} , to the soil carbon content as expressed by the octanol/water partition coefficient, K_{OW} (Fetter 1994; Baker 1997). Coefficient K_{OW} is defined as the ratio of the molar concentrations of a chemical in n-octanol and water, in dilute solution.

19.1.2 Principal Factors Affecting the Experimental Isotherm Data

Sorption effects determined by the type (shape) and parameters of sorption isotherms are controlled by the sorbent's properties and the chemistry of the pore solution. In general, sorption parameters for different geosorbents show close correlation with the clay and organic matter content, specific surface area, and cation exchange capacity. The high sensitivity of experiments to variations in these characteristics accounts for the contradictions in the literary data on the sorption of the same components on soils or aquifer materials of similar lithological varieties.

A variety of geochemical parameters of the pore solution affects the sorption characteristics as well. More or less reliable trends can be identified in the assessment of the effect produced on isotherm data by variations in some standard thermodynamic characteristics, such as ionic strength, pH, the composition of the solution with respect to the major (principal) anions and cations, which may compete with the contaminants for adsorption sites on the solid surface. The chemical properties of the solution in contact with the solid phase also affect the adsorption through interactions between dissolved species.

Thus, a characteristic case is the sorption of trace components (usually represented by heavy-metal ions and radionuclides) from solutions whose ionic strength is governed by major-cation concentrations (Appelo and Postma 2005). In this case, an increase in the ionic strength generally results in a decrease in the amount of the component adsorbed by the sediments or rock materials. This is because the increasing concentration in solution of the excessive cation, which occupies part of active sorption sites on the mineral surface, thus reducing the degree of its concentrating by the rock, creates the competition between this cation and the trace component being absorbed. At the same time, in solutions with high ionic strength, the activity (effective concentration) of the sorbed trace component drops, causing the effective sorption parameters to change in the same direction. More essentially, many trace-metal ions form complexes with principal anions in solution. The formation of these complex species can have a major influence on the charge and geometry of the original ion and as a result, significantly alter the sorptive properties of the trace ion of interest (Cantrell et al. 2002; Phillippi et al. 2007).

The interpretation of the effect produced on sorption by a dominating anion is less clear. However, if it is a priori acceptable to neglect the role of complex formation as a process enabling the solution to retain additional amount (as compared with the equilibrium ionic form) of the sorbed trace component chemically bound to the anion, the strongest effect will be produced by the specific adsorption of this anion. Out of the principal anions commonly considered in hypogeochimistry, such adsorption is typical of sulfate ions, SO_4^{2-} . The adsorption of SO_4^{2-} depends on pH (when the process follows anion exchange mechanism, i.e., the hydroxyl group is displaced from the exchange complex) and the organic matter content of rock soils or aquifer materials. The adsorption of SO_4^{2-} can enhance the surface potential of the geosorbents, thus intensifying the sorption of trace components.

The change of the acid-base state of the aqueous environment can have its effect on sorption capacity. It is of particular importance to consider this effect in the case of a linear isotherm. Thus, at low pH, active sites on the mineral phase of the rock that are able to adsorb the component are often occupied by protons, H^+ . An inverse situation can take place with organic pollutants: an increase in pH causes an increase in the degree of their ionization and their solubility, while their sorption capacity drops (Kargbo 1994).

The most detailed studies were focused on the sorption of radionuclides, such as Cs-137, Sr-90, Co-60, and actinoids (EPA 1999). Those studies revealed almost unlimited variation ranges of coefficient K_d of the linear model (19.1) – from a few tenths of unit to many thousands cm^3/g . Minimal values correspond to sandy and gravel sediment varieties, bearing high-salinity solutions, and maximal values, to clay varieties with diffusion-based saturation by low-salinity solutions. The variation range of K_a in fissured rocks is 0.1–100 cm.

Laboratory and field experiments supported by physicochemical modeling show that K_d values of most sorbed components in question are not invariant with respect to liquid phase geochemistry: even minor changes in the composition and temperature of solution cause abrupt and often nonmonotonic changes in K_d . Thus, the K_d values for metal ions typically vary over many orders of magnitude, depending on fluid pH and composition as well as the nature of the sediment (Bethke and Brady 2000).

Moreover, many authors note that the value of K_d may depend on the ratio of solution volume V to solid phase mass, m_s , V/m_s (the so-called liquid-to-solid ratio, L:S) in batch tests (Phillippi et al. 2007). Such dependence can be due to complex formation processes involving the studied component in solution. Another quite plausible cause is due to the fact that changes in L:S ratio affect the concentrations of exchange cations or dissolved salts, which have been initially contained in the subsurface materials and compete with the examined component for exchange sites (adsorption centers) on the solid phase. Therefore, it is particularly important to keep L:S ratio constant; otherwise, even qualitative comparison of results becomes incorrect. Hence, the liquid/solid ratio can be critical when extrapolating the results of batch experiments to column experiments and then to the field. These results have implications for modeling and predicting the reactive transport of contaminants in the subsurface environment (Phillippi et al. 2007).

The identification of sorption mechanisms and the occurrence forms of the examined component on mineral surfaces is a more complex problem. The *selective sorption method* (Zakharova et al. 2003; Sabodina et al. 2008) can be recommended for semiquantitative estimates. For example, according to this method, desorption from sediment samples is implemented by washing samples by different solutions, i.e., (1) water, (2) potassium chloride (1M), and (3) hydrochloric acid (1M). The use of other solutions is also possible (see Sects. 23.1.4 and 23.2.2). The percentage of radionuclides displaced from the rock matrix during washing by the three types of solutions is *conventionally* associated with the amounts of components in the solid phase that have been sorbed in accordance with the mechanisms of (1) physical sorption (adsorption), (2) ionic exchange, and (3) surface complex formation.

Of use can be sorption experiments at different pH of treatment solutions. For example, sorption of Cs-137 in bentonite and different fractions of clay sand was found to be weakly sensitive to changes in pH within the range from 3 to 10, while the adsorption rate of U(VI) and Np(V) under the same conditions showed an appreciable dependence on pH, suggesting that the ionic exchange mechanism dominates in the former case and surface complex formation dominates in the latter case (Sabodina et al. 2008). This conclusion was supported by studying sediment samples by selective desorption.

It is worth mentioning that an increase in K_d over time, which is often recorded in laboratory experiments and in monitoring data, can be attributed to the use of an equilibrium model for a process, which is actually kinetic. This effect is illustrated by data (e.g., Alonso et al. 2006), experimentally demonstrating the growth in K_d values over time for some radionuclides adsorbed by bentonite colloids.

A limitation on the use of conventional approaches to the description of adsorption processes is associated with their possible partial or complete irreversibility. This issue deserves special consideration.

19.1.3 Hysteresis Phenomenon in Sorption

19.1.3.1 Experimental Evidence

The study of the dynamics of processes governing the rehabilitation of groundwater quality in periods of natural or forced flow of water through contaminated areas (including sites of radioactive waste disposal) requires the development of models that consider possible hysteresis in sorption-related processes. By hysteresis is meant the difference between functions describing the sorption and desorption stages of migration process.

Sorption hysteresis in a sense of isotherm nonsingularity, slow desorption kinetics, and other nonideal phenomena, such as the irreversible alteration of sediments' minerals in contact with liquid waste (Sect. 23.2), may be attributed to the physical and chemical interactions of dissolved components with soils and aquifer materials. These phenomena explain the discrepancy between model prediction and field experience, related first of all to the analysis of remediation efficiency. Thus, contrary to model predictions, the water extracted during remediation characteristically contains a persistent "tail" of contaminants (Bethke and Brady 2000). Hysteresis in sorption is known to be of particular importance for colloid-facilitated transport under natural field conditions (Vilks et al. 1993; Kretzschmar et al. 1999; see also Sect. 24.3).

Sorption hysteresis has been a subject of considerable dispute among environmental researches over the past decades (Pickens et al. 1981; Vandergraaf and Abry 1982; Jackson and Inch 1983; Lyon and Patterson 1984; Vilks and Dequelare 1991; Streck et al. 1995; Wels et al. 1996; Rybalchenko et al. 1996, 1998; Zakharova et al. 1996; Rumynin et al. 1998; Lisitzin et al. 1999; Sander et al. 2005).

In recent decades, special attention was paid to studying the behavior of technogenic radionuclides in groundwater. To study the existence of hysteresis in radionuclide sorption, researchers have used batch sorption/desorption experiment (Vandergraaf and Abry 1982; Vilks and Dequellare 1991; Rybalchenko et al. 1998; Wels et al. 1996; Zakharova et al. 1996; Rumynin et al. 2002). Data on a low extent of desorption (a few percents to a few tens of percents) were reported in sorption/desorption studies of radionuclides, such as Cs-137, Sr-90, Ru-106, Ce-144, Pu-239 on sandy-clayey sediments (Rybalchenko et al. 1998; Zakharova et al. 1996). A relatively low percentage of desorption of radionuclides was recorded in experiments with volcanogenic-sedimentary rocks (Lisitzin et al. 1999). Low extraction of radionuclides was recorded for samples of soils taken within areas affected by the Chernobyl accident (Ovsyanikova et al. 2000).

In this context, the comparison of experimental partition coefficients for equilibrium sorption, K_d^s , and desorption, K_d^d , is of special interest for researchers. It was found that K_d values for desorption, K_d^d , for many contaminants were significantly higher than their sorption K_d values, K_d^s . This indicates that some irreversible adsorption processes may be taking place. Thus, Vilks and Dequellare (1991), who studied the behavior of Cs-137 and Sr-90 in colloidal systems, have found that K_d^d exceeds K_d^s (for Cs-137) by a factor of 4; no significant hysteresis was however found for Sr-90. Sorption interaction of ion IO_3^- with clay minerals (weathering products of granites that coat fractures) was characterized by the relation of K_d^d to K_d^s , which varied within the same range (Tiknor and Cho 1990).

Along with experiments aimed to study the sorption process in sediments with pore type of flow, one may find in the hydrogeological literature the results of experiments performed using rock coupons or rock cores that represent fractured rock formations. These studies showed that the mineralogical composition in rock fractures is very different from that in the rock matrix. Minerals typically encountered in fracture-filling materials include chlorite, calcite, epidote, fluorite, quartz, iron-oxyhydroxides, pyrite, clay minerals (e.g., kaolinite, smectite, and illite), and laumontite (Baik et al. 2010). Experiments with the surface material also often exhibit hysteresis in the sorption process.

Thus, batch sorption experiments with radionuclides (Sr-90, Cs-137, Ce-144, and Pu-237) on fracture surfaces (coupons cut from hard rock blocks) showed higher surface distribution coefficients for desorption, K_d^d , than for sorption, K_d^s (Vandergraaf and Abry 1982; Wels et al. 1996). The same effect was observed in similar experiments on sorption of Sr-90 onto surfaces of disks that were cut from the core material of volcanogenic and volcanogenic-sedimentary rocks (Rumynin et al. 1998).

In some investigations dedicated to the study of radionuclide sorption, a strong kinetic nature of the desorption stage was detected. Sufficiently prolonged periods of a change in the concentration function preceded a new desorption equilibrium. Thus, the relatively slow desorption kinetics of Sr-85 and Sr-90 was identified in field experiments and from analysis of residual radioactivity of cores of contaminated aquifer sediments by Pickens with co-investigators (1981). Expressed kinetics of Co-60 and Cs-137 desorption was observed in experiments with rocks

of metamorphic series (Fujikawa and Fukui 1991a, b). Considerable difference was found to exist between kinetic constants of desorption and adsorption on colloids for Am-241 (Van de Weerd and Leijnse 1997). The same trend was detected in experiments with uranium (VI) (in the form of uranyl, UO_2^{2+}) on hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (Mibus and Brendler 2005).

In the opinion of some authors (Rybalchenko et al. 1996; Zakharova et al. 1996), desorption kinetics of radionuclides, which at the sorption stage form strong chemical bonds with elements of crystal lattice, is controlled by “the mechanisms of leaching”. It was shown that a significant fraction (up to 70%) of Cs-137 is irreversibly lodged within clay particle matrices. The possibility of forming this type of chemical bonds is associated also with the manifestation of specific adsorption as established during a study of sandy cores at a radioactively contaminated site (Pickens et al. 1981; Jackson and Inch 1983). Experimental data showed that up to 15% of Sr-90 is held by a sediment in the specifically adsorbed (by hydroxides of iron and aluminum) state, and a strong correlation was established between the release of the residual Sr-90 and the content of extractable Fe, Al, and Mn in the sediment. The observed association of plutonium with Nevada Test Site colloids by Kersting et al. (1999), and many sorption experiments carried out in different laboratories indicate that the attachment of plutonium to colloids may be also an irreversible process.

In a number of experiments with radionuclides, however, only slight discrepancies between the sorption and desorption coefficients were detected (Aksoyoglu et al. 1990). Moreover, some researchers treat the hysteresis as an artifact: the non-coincidence of the sorption and desorption distribution coefficients is explained by a nonequivalence of experimental conditions at the stage of sorption and desorption; or by the equilibrium having not been reached by the system (Ma and Selim 1994; Streck et al. 1995) when the kinetically expressed process is interpreted within the framework of equilibrium models. As it was correctly noted by Lyon and Patterson (1984), who studied the nonequilibrium of Sr-90 sorption/desorption, some radionuclides, which cannot be desorbed in short-term laboratory experiments, can be removed over a period of 10–15 years in a groundwater flow system.

Some dissolved contaminants are known to absorb irreversibly from solution on solid substrate. Thus, detailed studies of sorption–desorption of cesium-137 on sediments typical of Hanford site, USA (Steeff et al. 2003), interpreted on the basis of models of equilibrium ion exchange on heterogenic sorption sites, showed a high (up to 90%) degree of reversibility of sorption process involving sediments rich in sodium nitrate (though, in one experiment, the reversibility factor was 73%). At the same time, the displacement of this cation from the polluted zone by infiltrating fresh water showed the sorption distribution coefficient so big that the process can be regarded as practically irreversible.

A factor of process irreversibility is the metastable state of the solid phase. For example, in the course of aging of newly deposited iron hydroxide, hydration reaction facilitates the transformation of the originally amorphous $\text{Fe}(\text{OH})_3(\text{s})$ into a crystalline salt $\text{FeOOH}(\text{s})$. Since this process is accompanied by surface restructuring, the components adsorbed before (e.g., heavy metal cations or radionuclides) can be incorporated into the crystalline structure of $\text{FeOOH}(\text{s})$ and hence cannot be desorbed (Banwart 1997).

By analogy, organic contaminants, such as pesticides, can have many common functional groups with natural organic matter in the soils and aquifer materials; therefore, they are involved in many one-type biological and chemical transformations, which are among the causes of irreversibility of sorption interactions (Berkowitz et al. 2008). Therefore, judging by literature data, the complete extraction of pesticides from soils is an exception, rather than a norm.

Overall, the identification of the type of sorption process (in particular, the degree of its irreversibility) and the identification of the parameters governing it are among the key tasks of experimental studies aimed at the examination of zones of polluted groundwater, which require rehabilitation. An evident fact in this case is the inapplicability of the “method of analogies,” because it is impossible to predict, basing on a priori assumptions, which of possible models will adequately describe the sorption interactions involving given components: the same component may behave quite differently in this respect under similar conditions.

19.1.3.2 A Dual-Site Model of Equilibrium Freundlich Sorption

Models of heterogeneous adsorption (reactive) sites are often used to describe sorption hysteresis (Selim and Amacher 1988; Jackson and Inch 1989; van Genuchten, Wagenet 1989; Ma and Selim 1994; Streck et al. 1995; Selim et al. 1976; Huang et al. 1998; Weber et al. 1998; Sharer et al. 2003; Steefel et al. 2003; Govindaraju and Das 2007). This approach allows the sorption interaction between different exchange sites of a mineral phase and dissolved matter to be described by different types of physicochemical reactions. The heterogeneity can be associated with homogeneous reactions on various adsorption centers, which however differ in the absolute values of parameters controlling these reactions.

For example, such a model has effectively been used to describe the hysteresis in adsorption of water-soluble hydrophobic organic compounds (pesticides, e.g., phenanthrene, simazine, and atrazine) on soils (Ma and Selim 1994; Streck et al. 1995; Šimůnek and van Genuchten 1995; Huang et al. 1998; Weber et al. 1998). These works explained the hysteresis by a low desorption rate and the heterogeneity of the sorption properties of the natural organic matter. The kinetic model of heterogeneous sorption sites has also shown good results in the processing of experiments on sorption–desorption of dissolved organochlorine compounds (Riley et al. 2006), trichloroethane (TCE) and tetrachloroethene (PCE). However, Burgos with coworkers (1999), who studied phenanthrene sorption on various soils, has shown that sorption hysteresis can be described by an equilibrium nonlinear model. They established that experimental points in coordinates $N = f(C)$ obtained at desorption stage can be closely approximated by the nonlinear Freundlich isotherm $N = K_F C^n$, where the exponent n for the four examined varieties varied within 0.48–0.63. Studies of the desorption of radionuclides adsorbed by clay minerals showed the same tendencies (see Sect. 22.6.2).

Some ideas in constructing models of heterogeneous sorption sites were developed in this study. Thus, a *phenomenological model* as described below assumes that reactive sites within solid environmental materials such as soils or aquifer

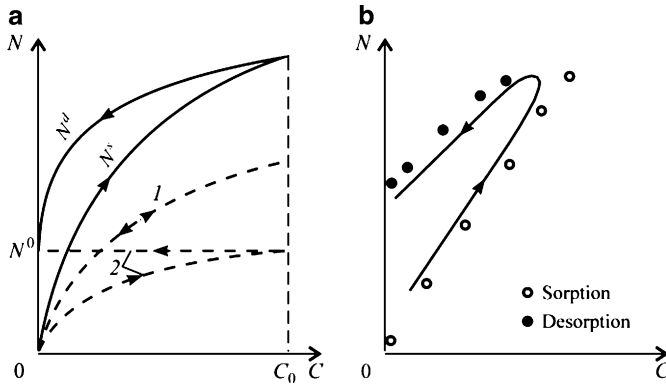


Fig. 19.1 Diagrams illustrating (a) two-site hysteresis-dependent sorption concept, and (b) a typical form of the plot of sorption–desorption batch experiment. (1) Eq. 19.6a, (2) Eq. 19.6b

materials can be divided into two fractions. Each fraction is responsible for a certain type of equilibrium physicochemical interactions between dissolved species and solid surface. These two types of sites may also differ in kinetic parameters controlling interactions between components presented in the liquid and solid phases (Sect. 19.2.2).

Let us assume that the interaction of components with sorption sites of *type 1* is governed by electrostatic adsorption, i.e. classical cation exchange (Jackson and Inch 1989; Sparks 2003), which implies components' ability to be easily absorbed and desorbed following one of the empirical isotherms, say, the Freundlich model (Fig. 19.1):

$$N_1^s = fK_1C^{n_1}, \quad N_1^d = fK_1C^{n_1}, \quad (19.6a)$$

where f represents the mass fraction of the sites where sorption is instantaneous and fully reversible, namely, the type 1 of the sites within the porous matrix.

We can then assume that the interaction of components with sorption sites of *type 2* is of *specific adsorption* nature, implying that chemical components enter a “Stern or Stern-like layer” at the interface (see Sect. 27.1) and form bonds with the mineral surface, which are stronger than electrostatic interactions at the sorbing sites of type 1. Apart from specific sorption, the absorbed components can be incorporated into the crystal structure to form a solid solution by other physicochemical mechanisms (Appelo and Postma 2005). Further we will assume that sorption of the components onto type 2 sorption sites is characterized by the same type of relationship between N and C , as in the first equation of Eq. 19.6a, however, when concentrations of the components in the solution decrease, their release from the sorption sites of type 2 back into the water does not occur due to the irreversibility of sorption:

$$N_2^s = (1-f)K_2C^{n_2}, \quad N_2^d = (1-f)K_2C_0^{n_2}; \quad (19.6b)$$

here and in (19.6a) N_1 and N_2 are the component concentrations in type 1 and type 2 sorption sites, respectively (superscripts s and d correspond to sorption

and desorption, respectively); $K_1 \equiv K_{F1}$ and $K_2 \equiv K_{F2}$ are the linear Freundlich coefficients for the two types of adsorption sites, respectively; n_1 and n_2 are the partial exponential constants for the two types of adsorption sites, respectively; C_0 is the concentration of a component in the solution at the beginning of the desorption step.

Specific adsorption is characterized by more selective and less reversible adsorption reactions involving chemisorbed inner-sphere complexes. The strong binding of metal ions with variable-charge soil minerals (e.g., oxides, allophane) and organic matter may retain and even immobilize heavy metals, whereas anionic metal complexes and oxy-anions may be selectively bound at variable-charge mineral surfaces and layer silicate particle edges (*Encyclopedia of Surface and Colloid Science et al. 2006*, p. 485).

The combined effect of the two forms of elementary acts of physicochemical interaction shows itself in the following total sorption–desorption isotherm:

$$N = \begin{cases} N^s = fK_1C^{n_1} + (1-f)K_2C^{n_2}, \\ N^d = fK_1C^{n_1} + (1-f)K_2C_0^{n_2}, \end{cases} \quad (19.7)$$

which is seen to have a hysteresis character (Fig. 19.1). Thus, the value of N depends not only on the current value of C , but also on the regime of C variations in the preceding time interval. The second equation in model (19.7) indicates that a contaminant desorption from sediments involves both fast-desorbing and no-desorbing fractions.

Sorption equation in system (19.7) differs from the Freundlich model (19.2); thus, the shape of the isotherm (19.7) is determined by linear coefficients, fK_1 and $(1-f)K_2$, as well as exponential coefficients, n_1 and n_2 . As one may see, the extent of component retention by geosorbent is a function of the concentration C_0 at the final sorption step

$$N^0 = (1-f)K_2C_0^{n_2}. \quad (19.8)$$

We mention in passing that in the linear sorption model $n_1 = n_2 = 1$, the partial coefficients K_1 and K_2 are related to the distribution coefficient K_d , conventionally determined in sorption experiments, by an obvious formula

$$fK_1 + (1-f)K_2 = \rho_b K_d, \quad (19.9)$$

where ρ_b is the bulk density of an aquifer material.

19.2 Models of Sorption/Desorption Kinetics

The kinetics of the sorption reactions can be controlled either by the actual thermodynamic reaction or by the transport mechanism in the porous media, which brings the reactants in contact with one another. In our further analysis, we will focus mostly on the first type of the sorption kinetics assuming that fluid flow velocity does not affect the interphase interactions.

19.2.1 Sorption Kinetics

An understanding of sorption kinetics can be gained from the basic equation for the total rate, v , of a chemical reaction

$$v = v_f - v_r \equiv \frac{\partial N}{\partial t}, \quad (19.10)$$

where v_f is the rate of forward (sorption) reaction and v_r is the rate of reverse (desorption) reaction.

Different hypotheses regarding the rate, v_f , at $v_r = k_r N$, yield one of the following expressions for the reaction rate:

$$\frac{\partial N}{\partial t} = \left\langle \begin{array}{c} k_f C - k_r N \\ k_f C^n - k_r N \\ k_f (N_v - N) C - k_r N \end{array} \right\rangle, \quad (19.11)$$

whence it follows that the “equilibrium” constants of major sorption isotherms, K (linear), K_F^s (Freundlich), and K_L (Langmuir), are the ratios of kinetic constants of the forward, k_f , and reverse, k_r , reactions $[T^{-1}]$: k_f/k_r (Selim 1989; Van den Brink and Zaadnoordijk 1997; Zhou and Selim 2001).

Therefore, all kinetic relationships for reversible sorption given above can be combined into the linear equation

$$\frac{\partial N}{\partial t} = \alpha(N^{\text{eq}} - N), \quad N^{\text{eq}} = f(C); \quad (19.12)$$

here N^{eq} is the equilibrium concentration of the substance on the solid phase, corresponding to its current concentration in solution, C , and related to the latter by an isothermal relationship, $f(C)$; α is the first-order rate constant, which formally is the reverse rate constant, k_r . In accordance with (19.12), the sorption rate is determined by the degree of deviation of the physicochemical system from the equilibrium state.

19.2.2 A Generalized Nonequilibrium Sorption Model

Nonequilibrium sorption models are of special interest for the description of hysteresis effects that may be observed during an absorption–desorption cycle. In hydrogeological practice, the development of relevant models motivates the necessity of quantifying sorption behavior during a natural attenuation or remediation phase related to overall migration processes at contaminated sites. Dual-site (or more general multi-site) sorption models seem to be quite adequate to address this subject. Indeed, a number of investigations have indicated that contaminant desorption from sediments involves the release of the contaminant from both fast-desorbing

and slow-desorbing geosorbent fractions associated with two types of reactive sites. The fast-desorbing fraction requires only minutes or hours for desorption, while the slow-desorbing fraction releases the contaminant over periods of months to years.

Following the initial hypothesis introduced in Sect. 19.1.2, we assume that two types (i.e., types 1 and 2) of reactive sites exist in a representative volume of the porous media. These two types of sites differ in equilibrium and kinetic parameters controlling interactions between components presented in the liquid and solid phases. If the sorption process is under the conditions of a local equilibrium and obeys the Freundlich isotherm (19.2), then the sorption kinetics on the two types of the reactive sites can be described as follows:

$$f \frac{\partial N_1}{\partial t} = \alpha_1^s (K_1 C^{n_1} - N_1), (1 - f) \frac{\partial N_2}{\partial t} = \alpha_2^s (K_2 C^{n_2} - N_2), \quad (19.13a)$$

where C is the concentration of the sorbed component in solution; N_1 and N_2 are concentrations on the solid phase (for type 1 and type 2 sites, respectively); K_1 and K_2 are the partial linear Freundlich constants; n_1 and n_2 are the partial exponential constants; α_1^s and α_2^s are the first-order rate constants; f is the fraction of the site 1 (corresponding to a portion of the first type of the sites within the porous matrix).

The corresponding equations for the desorption are as follows:

$$f \frac{\partial N_1}{\partial t} = \alpha_1^d (K_1 C^{n_1} - N_1), (1 - f) \frac{\partial N_2}{\partial t} = \alpha_2^d (K_2 C^{n_2} - N_2), \quad (19.13b)$$

where α_1^d и α_2^d are the first-order rate constants for desorption stage.

This model can be seen to take into account the possible difference between the kinetic constants of sorption and desorption. The system of Eqs. 19.13 is multi-parametric, i.e., it is characterized by a set of parameters, reflecting the different interaction rate (equilibrium and kinetic) between the dissolved components and the components adsorbed on different types of adsorption sites (at both adsorption and desorption stages). In particular, assuming $\alpha_i^d < \alpha_i^s$, we can simulate slower desorption kinetics. In limiting variants we have: (1) when α_1^d or $\alpha_2^d \rightarrow 0$, we come to the case of irreversible adsorption on sites of one of the types; (2) when $\alpha_{1,2}^s, \alpha_1^d \rightarrow \infty, \alpha_2^d \rightarrow 0$, we come to the case of equilibrium, partially irreversible adsorption considered in the previous case.

19.3 Models for Static (Batch) Sorption Experiments

19.3.1 Mass Balance in a Batch Experiment

The total mass of a component in a closed system can be written as

$$M^T = VC + N(m_s/\rho_b), \quad (19.14)$$

where V is the volume of the solution, C is the component's concentration in solution, m_s is the weight of the geosorbent sample, ρ_b is the bulk dry density, N is the total component's concentration in the solid phase:

$$N = fN_1 + (1 - f)N_2. \quad (19.14a)$$

Equation 19.15 describes the mass balance in a batch experiment:

$$\frac{dM^T}{dt} = 0, \text{ or,} \quad (19.15)$$

$$a \frac{dC}{dt} + \frac{dN}{dt} = 0, \quad a = \frac{V \rho_b}{m_s}. \quad (19.15a)$$

The system of Eqs. 19.13, 19.13a, and 19.15a is closed when the initial conditions ($t = 0$) are assumed as follows:

$$N_1 = N_2 = 0, C = C_i - \text{at the sorption stage,} \quad (19.16)$$

$$N_1 = N_{i1}, N_2 = N_{i2}, C = 0 - \text{at the desorption stage,} \quad (19.16a)$$

where C_i is the initial concentration of the adsorbing component in the solution, N_{i1} and N_{i2} are the initial concentrations of the component on the sorption sites upon substitution of the solution.

For solving the system of the differential Eqs. 19.13a, 19.13b, and 19.15a, a numerical algorithm using a finite difference solution method was developed.

19.3.2 *One-Site Kinetic Model of Sorption with Concomitant Mineral Dissolution*

Sorption experiments are often accompanied by the appearance in solution of the products of dissolution and transformation of minerals, primarily, carbonates, which are not directly involved in sorption of the examined components (see Sect. 19.1). The dissolution products can be represented, for example, by ions of calcium, magnesium, and stable strontium, which compete with the examined component for adsorption sites in the adsorption (ion-exchange) complex of soil or aquifer material. This changes the ratio between the latter's concentrations in liquid and solid phases, and this fact should be taken into account in the models used to interpret the laboratory experiments.

An influence of the cations, which are present in the solution in "macro-quantities", on the adsorption of Sr-90 and Cs-137 was observed in numerous previous experiments (e.g., Kokotov and Popova 1962; Liszewski and Bunde 1998; EPA 1999). These experiments used prepared solutions, which initially contained cations of the mentioned bivalent metals. In this section, we show how variations

in main component concentrations resulting from the rate-limited dissolution of the mineral phase can affect the kinetically-controlled sorption and desorption.

The assumptions for the analysis provided in this section are that (1) the adsorption process is ion-exchange, (2) the mineral dissolution produces cations that compete for adsorption (ion exchange) sites with the radionuclide, (3) radionuclide concentrations on a mineral phase are much lower than those of the total exchange capacity, N_v .

In accordance with the law of mass action, the ion-exchange equilibrium in the two-component system is determined by the equation (Charbeneau 1982):

$$K_{12} = \left(\frac{N_1}{C_1} \right)^{z_2} \left(\frac{C_2}{N_2} \right)^{z_1}, \quad (19.17)$$

where C_1 and C_2 are the concentrations of the displacing cation of radioactive metal (1) and of the displaced cation of stable component in the solution (2), respectively; N_1 and N_2 are the concentrations of the radionuclide and the stable component on solid surfaces, respectively; K_{12} is the selectivity coefficient for the cation-exchange reaction between 1 and 2; and z_1 and z_2 are the corresponding charges of cations.

Assuming $N_v = N_1 + N_2$ and $N_1 \ll N_2$ (i.e., that the concentration of radionuclides on the solid phase is significantly smaller than the concentration of the displaced cation), Eq. 19.17 becomes:

$$N_1 = \frac{C_1}{K_s C_2^{\bar{z}}} \quad (\bar{z} = z_1/z_2, \quad K_s = (K_{12} N_v^{z_1})^{-1/z_2}). \quad (19.18)$$

The validity of these assumptions and Eq. 19.18 was confirmed experimentally during a study on the influence of calcium ions on the calculated values of the Sr-90 distribution coefficient, K_d (Yegorov et al. 1961; Kokotov and Popova 1962). A strong inverse linear relationship between the adsorbed strontium and calcium + magnesium concentrations in solution was also noted in experimental work by Liszewski et al. (1998).

In this case, the equation describing the sorption kinetics can be written as

$$\frac{dN_1}{dt} = \alpha_1 (C_1 - K_s C_2^{\bar{z}} N_1), \quad (19.19)$$

where α_1 is the kinetic constant.

A mass balance equation for the construction of a model for batch experiment interpretation is as follows:

$$\frac{dM^T}{dt} = 0, \quad M^T = VC_1 + N_1(m_s/\rho_b), \quad (19.20)$$

$$a \frac{dC_1}{dt} + \frac{dN_1}{dt} = 0, \quad (19.21)$$

where V is the volume of the solution, m_s is the weight of the sediment sample, ρ_b is the dry bulk density, and $a = V\rho_b/m_s$.

Radionuclide concentration on the solid phase (N_1) for two stages of the experiment (sorption and desorption) can be presented as follows:

$$N_1 = a(C_1^0 - C_1), \text{ for sorption,} \quad (19.22)$$

$$N_1 = N_0 - aC_1, \text{ for desorption,} \quad (19.23)$$

where C_1^0 is the initial (before the sorption stage) radionuclide concentration in solution; $N_0 = a(C_1^0 - C_1^*)$ is the concentration of the radionuclide on the sediment before desorption; C_1^* is the concentration which was measured at the end of the adsorption step.

Substituting Eqs. 19.21, 19.22, and 19.23 into the kinetic Eq. 19.19, we obtain the following equations:

$$\frac{dC_1}{dt} = \alpha_1 \left[K_s C_2^{\bar{z}} C_1^0 - \left(\frac{1}{a} + K_s C_2^{\bar{z}} \right) C_1 \right] \text{ for sorption,} \quad (19.24)$$

$$\frac{dC_1}{dt} = \alpha_1 \left[K_s C_2^{\bar{z}} \frac{N_0}{a} - \left(\frac{1}{a} + K_s C_2^{\bar{z}} \right) C_1 \right] \text{ for desorption.} \quad (19.25)$$

Considering a dissolution reaction that proceeds in parallel to the sorption reaction and which is presented by a first-order rate equation (Golubev 1981):

$$C_2 = C_2^{\text{sat}} - (C_2^{\text{sat}} - C_2^0) e^{-\alpha_2 t}, \quad (19.26)$$

where C_2^0 is the initial concentration of the cation in the solution, C_2^{sat} is the concentration at saturation, and α_2 is the kinetic dissolution constant of the mineral.

The initial conditions ($t = 0$) for the proposed experimental setup are:

$$\begin{aligned} N_1 = 0, \quad C_1 = C_1^0, \quad C_2 = C_2^0 & \text{ for the sorption stage,} \\ N_1 = N_0, \quad C_1 = 0, \quad C_2 = C_2^0 & \text{ for the desorption stage.} \end{aligned} \quad (19.27)$$

Equations 19.24 and 19.25 can be rewritten in a generalized dimensionless form:

$$\frac{d\bar{C}_1}{d\bar{t}} = \left[(\bar{C}_2^0 \bar{C}_2)^{\bar{z}} - \left(\frac{1}{a} + (\bar{C}_2^0 \bar{C}_2)^{\bar{z}} \right) \bar{C}_1 \right], \quad (19.28)$$

where $\bar{C}_1 = C_1/C_1^0$ for the sorption process and $\bar{C}_1 = aC_1/N_0$ for the desorption process.

A dimensionless form of Eq. 19.26 is

$$\begin{aligned} \bar{C}_2 = \bar{C}_2^{\text{sat}} - (\bar{C}_2^{\text{sat}} - 1) e^{-\bar{\alpha} \bar{t}} \left(\bar{C}_2 = \frac{C_2}{C_2^0}, \bar{C}_2^{\text{sat}} = \frac{C_2^{\text{sat}}}{C_2^0} \right); \\ \bar{C}_2^0 = K_s^{z_2/z_1} C_2^0 \left(K_s^{z_2/z_1} = \frac{1}{K_{12}^{1/z_1} N_v} \right); N_0 = a(C_1^0 - C_1^*); \bar{t} = \alpha_1 t; \bar{\alpha} = \alpha_2/\alpha_1. \end{aligned} \quad (19.29)$$

The transformed initial conditions (19.27) are:

$$\begin{aligned}\bar{N}_1 &= 0 & \bar{C}_1 &= 1 & \bar{C}_2 &= 1, \\ \bar{N}_1 &= 1 & \bar{C}_1 &= 0 & \bar{C}_2 &= 1,\end{aligned}\tag{19.30}$$

where

$$\bar{N}_1 = N_1/N_0.$$

Thus, the problem can be reduced to the solution of the following first-order ordinary differential equation:

$$y' + f(\bar{t}) y = g(\bar{t}),\tag{19.31}$$

where

$$y \equiv y(\bar{t}) = \bar{C}_1, \quad f(\bar{t}) = \frac{1}{a} + (\bar{C}_2^0 \bar{C}_2)^{\bar{z}}, \quad g(\bar{t}) = (\bar{C}_2^0 \bar{C}_2)^{\bar{z}}.$$

Equation 19.31 can be solved with the help of a substitution $y = uv$, which leads to the transformation of Eq. 19.31 as follows:

$$u'v + u[v' + v f(\bar{t})] = g(\bar{t}).\tag{19.32}$$

As one of the supplementary functions (u or v) can be taken arbitrary, we can consider v as some particular integral of Eq. 19.33:

$$v' + v f(\bar{t}) = 0, \quad \frac{dv}{v} = -f(\bar{t}) d\bar{t}.\tag{19.33}$$

Then for finding the u -function, we have Eq. 19.34:

$$u'v = g(\bar{t}).\tag{19.34}$$

Integrating Eq. 19.33 we obtain:

$$v = v_0 e^{-F(\bar{t})}, \quad v_0 = v(\bar{t} = 0), \quad F(\bar{t}) = \int_0^{\bar{t}} f(x) dx.\tag{19.35}$$

Accordingly, the solution of Eq. 19.34 is:

$$u = u_0 + \frac{1}{v_0} \int_0^{\bar{t}} g(x) e^{F(x)} dx, \quad u_0 = u(\bar{t} = 0).\tag{19.36}$$

Finally,

$$y = uv = e^{-F(\bar{t})} \left[u_0 v_0 + \int_0^{\bar{t}} g(x) e^{F(x)} dx \right].\tag{19.37}$$

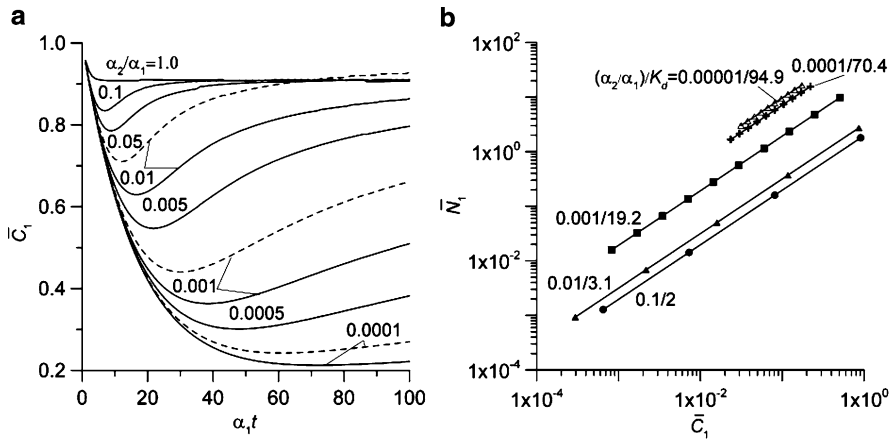


Fig. 19.2 Calculated curves reflecting (a) the combined influence of component sorption and mineral dissolution under unsteady-state condition (solid lines are for $\bar{C}_2^{\text{sat}} = 50$, dotted lines are for $\bar{C}_2^{\text{sat}} = 100$), and (b) calculated desorption isotherms, $\alpha_1 \Delta t = 100$. Calculations were carried out with $a = 20$ and $\bar{C}_2^0 = 0.01$

As $u_0 v_0 \equiv y_0$ is the initial concentration for $\bar{t} = 0$, then $u_0 v_0 = 1$ for sorption, and $u_0 v_0 = 0$ for desorption.

Thus, the general solution of Eq. 19.28 becomes

$$\bar{C}_1 = e^{-F(\bar{t})} \left[1 + \int_0^{\bar{t}} g(x) e^{F(x)} dx \right], \quad (19.38)$$

$$\bar{C}_1 = e^{-F(\bar{t})} \int_0^{\bar{t}} g(x) e^{F(x)} dx \quad (19.38a)$$

for the sorption ($\bar{C}_1 = C_1/C_1^0$) and desorption ($\bar{C}_1 = aC_1/N_0$) steps of the process, respectively.

Figure 19.2a presents kinetic sorption curves that were calculated for the exchange of univalent cations over a wide range of the dimensionless parameter $\bar{\alpha} = \alpha_2/\alpha_1$ for specified values $\bar{C}_2^{\text{sat}} = \bar{C}_2^{\text{sat}}/\bar{C}_2^0$, $\bar{C}_2^0 = K_s \bar{C}_2^0$ and $a = V \rho_b / m_s (\bar{z}_1 = 1)$. In the general case ($10^{-4} < \bar{\alpha} < 1$), graphs are essentially non-monotonic. The presence of a concentration minimum is explained by the competition of two reactions as discussed earlier. At the first stage, the solid/mineral phase actively adsorbs the component and the concentration function $C_1(t)$ decreases. However, later, the dissolution of minerals leads to the accumulation in solution of the competing cation and the latter starts displacing the earlier adsorbed component from the solid/mineral so that the cation's concentration in solution starts increasing.

Two limiting cases may be associated with the asymptotic behavior of the function $\bar{C}_1$:

1. if $\bar{\alpha} \ll 1$ then $\bar{C}_1 = \frac{a\bar{C}_2^0}{1 + a\bar{C}_2^0}$

(i.e., dissolution proceeds slowly and practically does not influence the adsorption) and

2. if $\bar{\alpha} \gg 1$ then $\bar{C}_1 = \frac{a\bar{C}_2^0\bar{C}_2^{\text{sat}}}{1 + a\bar{C}_2^0\bar{C}_2^{\text{sat}}}$

(i.e., the rapid mineral dissolution leads to a quick saturation of the solution with the competing cation, which significantly suppresses the sorption of the radionuclide).

In our example (Fig. 19.2a), the lower limiting value ($\bar{\alpha} \ll 1$) of $\bar{C}_1$ is 0.17 and the upper limiting values ($\bar{\alpha} \gg 1$) are 0.91 and 0.95 for $\bar{C}_2^{\text{sat}} = 50$ and $\bar{C}_2^{\text{sat}} = 100$, respectively.

Graphs of the step-by-step radionuclide desorption in the presence of a kinetically dissolving mineral are of some interest as well (Fig. 19.2b). According to the theoretical analysis, the calculated (effective) constant of the desorption distribution $\bar{K}_d$ (dimensionless parameter) ranges from $\bar{K}_d = (K_s C_2^0)^{-1}$ ($\bar{\alpha} \ll 1$) to $\bar{K}_d = (K_s C_2^0 \bar{C}_2^{\text{sat}})^{-1}$ ($\bar{\alpha} \gg 1$). The model isotherms are also controlled by the relationship of the kinetic constants $\bar{\alpha} = \alpha_2/\alpha_1$. Thus, in our example (Fig. 19.2b), the fitting constant of the desorption distribution $\bar{K}_d$ ranges from 94.9 when $\bar{\alpha} = 10^{-5}$ to 2.0 when $\bar{\alpha} = 0.1$. The value of $\bar{K}_d$ depends on the duration of the sorption and desorption steps Δt as well.

Lastly, a drop in the saturation concentration C_2^{sat} from one desorption step to the next leads to localization of the desorption points (N_i^d , C_i^d) on lines in coordinates N – C , which can be associated with nonlinear desorption isotherms (Fig. 19.3). This nonlinearity was noted in a number of experimental series. The observed hysteresis

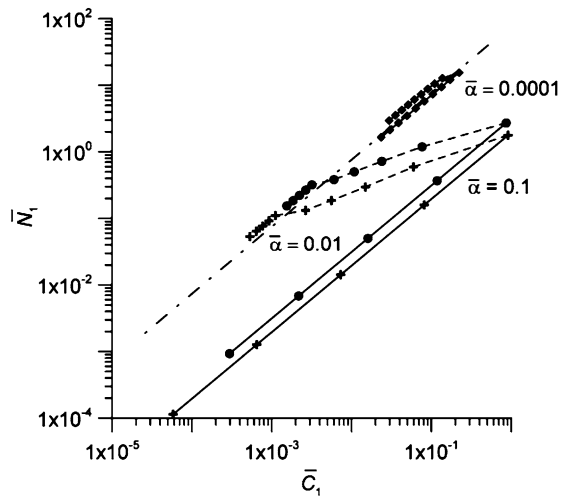


Fig. 19.3 Calculated desorption isotherms with $a = 20$, $\bar{C}_2^0 = 0.01$, $\alpha_1 \Delta t = 100$. Solid lines are for $\bar{C}_2^{\text{sat}} = 50 = \text{const}$, dotted lines are for $\bar{C}_2^{\text{sat}} = \bar{C}_2^{\text{sat}}(i)$: $\bar{C}_2^{\text{sat}}(1) = 50$, $\bar{C}_2^{\text{sat}}(2) = 10$, $\bar{C}_2^{\text{sat}}(3) = 5$, $\bar{C}_2^{\text{sat}}(4) = 3$, $\bar{C}_2^{\text{sat}}(5) = 2$, $\bar{C}_2^{\text{sat}}(6) - \bar{C}_2^{\text{sat}}(10) = 1$

depends in this case on both variations in the values of C_2^{sat} and on kinetics of the sorption and dissolution processes. For example, if the desorption step of an experiment is characterized by a lower value of concentration C_2^{sat} (compared with C_2^{sat} of the sorption stage), then the value of $\bar{K}_d$ will be greater than what is predicted for the sorption stage.

The described effect is often encountered in practice. A decrease in the “effective” values of C_2^{sat} from one experimental step to the next is explained by the gradual wash-out from sediments with a limited content of soluble salts (minerals).

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Chapter 20

Conceptual Transport Models for Adsorbable Solutes

In order to study non-conservative contaminant transport, it is essential to couple physicochemical phenomena with flow and transport models. The analytical solutions presented here combine equations for groundwater flow along streamlines with equations for sorption (both linear and nonlinear, equilibrium and first-order kinetic) processes and first-order decay. A simplified radionuclide transport model accounting for the effect of the presence of stable trace components in the formation water on sorption is also considered.

20.1 Equilibrium Sorption in Groundwater Flow

In this section, we will assume that the migrating component is sorbed by aquifer material instantaneously, i.e. fast enough not to be influenced by the solute-migration velocity.

20.1.1 *Effective Transfer Parameters for Equilibrium Reversible Sorption*

20.1.1.1 Effective Porosity and Retardation Factor

If sorption from solution is described by a linear or nonlinear convex isotherm, $N = f(C)$, then the initially piston-like concentration front advances without change of shape (Rachinsky 1964; Charbeneau 1981; Venitcianov and Rubinshtein 1983). Setting up matter balance equation for any streamtube, as it was made in (Charbeneau 1981; Golubev 1981; Shestakov 1995), we come to the expression for the actual fluid velocity of a component being sorbed:

$$u^s = \frac{q}{\phi + \Delta\phi} \left(\Delta\phi = \frac{\Delta N(C)}{\Delta C} \right); \quad (20.1)$$

here $\Delta C = C_0 - C^0$, $\Delta N = N_0 - N^0$; N_0 and N^0 are the concentrations of a component in the solid phase that are in equilibrium with the boundary, C_0 , and initial, C^0 , concentrations in the solution ($C_0 > C^0$). Thus, sorption can be accounted for in various relationships for piston-like displacement by replacing the active porosity, ϕ , by the *effective porosity*

$$\phi_e = \phi + \Delta\phi, \quad (20.2)$$

which is also called the *soil, sediment or rock material capacity factor*.

Thus, for linear, Henry isotherm (19.1), $\Delta\phi = K_d \rho_b$ ($\Delta\phi = K_a S_b$ in fractured rocks), while for Langmuir isotherm (19.3), $\Delta\phi = KN_v / (1 + KC_0)(1 + KC^0)$, $N_v = N_{\max} S_b$ in fractured rocks.

In some cases, it is more convenient to describe sorption in groundwater flow with the use of the parameter

$$R = 1 + \frac{\Delta\phi}{\phi} = 1 + \frac{\Delta N}{\phi \Delta C}, \quad (20.3)$$

referred to as the *retardation factor*. In the case of linear sorption,

$$R = 1 + \frac{K_d \rho_b}{\phi} \quad \text{or} \quad R = 1 + \frac{K_a S_b}{\phi}, \quad (20.3a)$$

for porous sediments or fractured rocks, respectively.

The retardation factor, Eq. 20.3a, represents the ratio between the advective velocity of water, u , and the average velocity of the front of a reacting (sorbing) solute, u^s : $R = u/u^s$.

In this case, the general solution of the one-dimensional advective-transport equation will have the following formal representation:

$$C(x, t) = C^0 + (C_0 - C^0)H(u^s t - x), \quad (20.4)$$

where H is the step-wise Heavyside function.

Nonlinear sorption processes in a bed with appreciable development of dispersion phenomena are more difficult to describe. In this case, it is helpful to use the sorption isotherm to relate the rate of component sorption from solution, W_s , with the rate of changes in the mass flux in pores:

$$W_s = \frac{\partial N}{\partial t} = f' \frac{\partial C}{\partial t}, \quad (20.5)$$

where $f' \equiv f'(C) = \frac{d}{dC} f(C)$ is the derivative of the sorption isotherm with respect to concentration in a point with equilibrium concentration of component C . Substituting (20.5) into the general transport equation (1.25) allows us to eliminate the variable W_s from it:

$$R(C) \frac{\partial C}{\partial t} + \nabla \cdot (\mathbf{u}C) - \nabla \cdot (\mathbf{D} \cdot \nabla C) = 0, \quad (20.6)$$

where $R(C)$ is an concentration-dependent (time-dependent) retardation factor, accounting for an increase in the storage capacity of the system and the retardation of solute migration velocity,

$$R(C) = 1 + f'(C)/\phi. \quad (20.6a)$$

Thus, in the general case of nonlinear sorption isotherms, R depends on the concentrations and may change over time and space. In particular,

- for Freundlich sorption isotherm

$$f' = nK_F C^{n-1}, \quad (20.7a)$$

- for Langmuir sorption isotherm

$$f' = N_v K_L / (1 + K_L C)^2, \quad (20.7b)$$

- for Tóth sorption isotherm

$$f' = N_v K'_L / [1 + (K'_L C)^{\beta_T}]^{1+1/\beta_T}. \quad (20.7c)$$

In the case of sorption, described by a linear isotherm (19.1), $f' = \rho_b K_d = \text{const}$, i.e., in all models for microdispersion, sorption following linear law can be accounted for by formal inclusion of the retardation factor, $R = \text{const}$, in the model (20.6).

The character of influence of nonlinear sorption on the migration regime is largely governed by the type of isotherm (see Sect. 1.5). Thus, in the case of a *convex* isotherm (the derivative f' decreases with concentration), sorption capacity will be larger for the points of the concentration front with a relatively low concentration of the component. The result is that the isolines with higher concentrations move faster and the width of the transitional zone tends to decrease with time (the case of $C_0 > C^0$). Thus, in one-dimensional solute transport, two factors act in opposite directions: the first – longitudinal dispersion – tends to “dilute” the front, while the second – sorption – contributes to its compaction. These two trends made it possible to hypothesize that the two mechanisms can cancel out at some stage of the transport, corresponding to asymptotic regime (Venitcianov and Rubinshtein 1983; Bosma and van der Zee 1993; Vanderborght et al. 2005): the front shows a parallel displacement (the dispersion zone does not decrease) with a constant velocity.

From here it follows that nonlinear sorption of this type can have a favorable effect on the transport of pollutants that are hazardous even in small concentrations (such as radionuclides): because of nonlinearity of the process, the most advanced part of the pollutant plume will be suppressed. On the other hand, in the case of impulse or square-pulse input concentration signal, the rear front of the concentration wave moves with a lower velocity, such that the appropriate concentration points fall more and more behind the front of peak values, in particular, the breakthrough

curves $C = f(t)$ demonstrate obvious “tail effects”. It is clear, therefore that the manifestation of nonlinear sorption in dynamic experiments can be misinterpreted as an effect of sorption kinetics on migration process.

When the isotherm is *concave*, both factors – the mechanical dispersion and nonlinear sorption – act in the same direction (the case of $C_0 > C^0$). However, considering that dispersion causes the extension of the front with a velocity proportional to $\sqrt{t}$ (one-dimensional migration flows), while the nonlinearity of sorption process extends the transitional zone with a velocity proportional to t , one can suppose that the contribution of longitudinal hydrodynamic dispersion to the total process of frontal zone extension will become insignificant over time (Venitcianov and Rubinshtein 1983).

In the case of desorption of previously adsorbed components (the case of $C_0 < C^0$), the character of development of concentration fields over time for the cases of convex and concave isotherms changes to the opposite relative to the regularities considered above. It is important that the superposition of sorption and desorption waves that takes place, in particular, after a change in the boundary concentration contributes to the suppression of total concentration perturbation and the significance of such effects can be higher than that of the dispersion-induced smoothing of maximal concentrations.

20.1.1.2 On Limitations of the K_d Approach

The applicability of the discussed above single-component isotherm approach to describing contaminant transport processes can be illustrated by the linear model given by Eqs. 20.3/20.6. In this model the interactions of solute with solid phases are bulked into a simple distribution coefficient, K_d (or into a retardation factor, R). The incorporation of the K_d -term (or R -term) into a solute transport model is called *K_d approach* or *concept*. As indicated previously (Sect. 19.1.2), the primary drawback of this approach is that the model is purely empirical and should be applied only to the conditions under which K_d was measured (Cantrell et al. 2002; Steefel et al. 2003; Phillippi et al. 2007); this follows from the fact that K_d 's most studied sorbing components are not invariant with respect to liquid-phase (pore solution) geochemistry.

One may expect the most significant discrepancies to exist between the results of a reactive transport model calculated using K_d approach and real field data dealing with remediation technologies and natural attenuation of contaminated sites (Bethke and Brady 2000). Flushing the contaminated zone with fresh water (whether during active remediation or by natural recharge) creates the hydrogeochemical conditions that vary dramatically over time and space. Under such conditions, it becomes impossible to choose some average and unique value for the distribution coefficient, K_d , to adequately describe the behavior of the advancing and falling edges of the concentration wave in different moments. Flushing the contaminated zone with fresh water gradually displaces dissolved and sorbed contaminants from the aquifer,

and the process exhibits a strong tailing effect maintaining the concentrations of contaminants below drinking water standards. The K_d approach, in contrast, predicts that flushing should efficiently displace all of the contaminants, both sorbed and dissolved, leaving the aquifer clean (Bethke and Brady 2000).

These facts have determined the recent active criticism of the K_d concept and stimulated the development of more advanced approaches to describing this class of physicochemical interactions accompanying solute migration (Bethke and Brady 2000). Thus, an alternative to the above effective model of physical sorption can be multicomponent multi-site (MCMS) reactive transport models with ion-exchange and surface complexation types of reactions (see Sect. 27.1). Although most of the mechanisms that govern surface sorption are fairly well understood, data are not readily available for all the contaminants, sorbents, and hydrogeochemical conditions required for MCMS transport model design (Cantrell et al. 2002). Therefore their practical application faces serious difficulties in getting verifiable results. Note some of them.

First, the choice of the model type that will adequately describe the sorption interaction between solution components and the real rock with polymineral composition often requires one to analyze the process at the levels of molecules or atoms (Fédoroff and Lefèvre 2006; Berkowitz et al. 2008, p. 96) with the involvement of various (commonly very expensive) laboratory equipment and highly qualified experts. The resources required to develop these data would be very large in terms of both cost and time.

Second, in the interaction with real rock, represented by a polymineral mixture, sorption reactions may have different rates at different mineral surfaces, be governed by different mechanisms, and proceed via several schemes, thus making it even more difficult to interpret experimental results and to choose the preferable MCMS model.

Third, the application of the MCMS approach is restricted by a variety of irreversible and rate-controlled processes known to impact adsorption at some sites, many of these kinetic processes being poorly quantified, resulting in difficulties with verification, validation, and calibration of such models.

To all appearance, the traditional approach based on a linear K_d (or other single-component isothermal) model has the advantages of being simple and universal with viewpoint of coupling sorption with other migration mechanisms, and these advantages are supported by the database development for a specific site in which K_d values are determined over a range of geochemical parameters that have the greatest influence on sorption. Another approach involving a variety of software programs for reactive transport modeling might serve to examine the applicability of K_d -based models. At least, projects related to forecasting groundwater contamination by hazardous wastes, e.g. containing radionuclides, require some additional efforts to describe the sorption process in a fashion more realistic than the K_d approach allows (Bethke and Brady 2000).

20.1.2 The Influence of Nonlinear Sorption on Advective–Dispersive Solute Transport

As mentioned in Sect. 20.1.1.1, the differently directed effect of hydrodynamic dispersion and nonlinear sorption (convex isotherm, $C_0 > C^0$) creates the conditions for the formation of a stationary concentration front, all points of which move with the same constant speed. Such asymptotics of the process justifies the search for the solution of the boundary value problem in the form of a travelling wave (Rachinsky 1964; Venitcianov and Rubinshtein 1983, p. 139; Polyanin et al. 2005); see also Sect. 1.5.1. In the one-dimensional formulation, the general solution becomes

$$C(x, t) = C(\eta), \quad N(x, t) = N(\eta), \quad (20.8)$$

where η is a moving coordinate

$$\eta = x - u^s t \quad (20.8a)$$

(u^s is the constant velocity of displacement of all concentration points within the boundaries of the transitional zone), such that

$$\frac{\partial C(x, t)}{\partial t} = \frac{\partial \eta}{\partial t} \frac{dC(\eta)}{d\eta} = -u^s \frac{dC(\eta)}{d\eta}, \quad \frac{\partial N(x, t)}{\partial t} = -u^s \frac{dN(\eta)}{d\eta}, \quad (20.9a)$$

$$\frac{\partial C(x, t)}{\partial x} = \frac{\partial \eta}{\partial x} \frac{dC(\eta)}{d\eta} = \frac{dC(\eta)}{d\eta}, \quad (20.9b)$$

$$\frac{\partial^2 C(x, t)}{\partial x^2} = \frac{\partial}{\partial x} \left(\frac{\partial C(x, t)}{\partial x} \right) = \frac{\partial}{\partial x} \left(\frac{dC(\eta)}{d\eta} \right) = \frac{\partial \eta}{\partial x} \frac{\partial}{\partial \eta} \frac{dC(\eta)}{d\eta} = \frac{d^2 C(\eta)}{d\eta^2}. \quad (20.9c)$$

In this case, the governing Eq. 20.6 (one-dimensional representation) becomes

$$[u - R(C)u^s] \frac{dC}{d\eta} = D_L \frac{d^2 C}{d\eta^2}. \quad (20.10)$$

During long stages, the effect of the input boundary of the flow on mass transport can be neglected (*asymptotic regime*); therefore, the problem can be reduced to the consideration of the process in an unbounded medium ($-\infty \leq \eta \leq \infty$)

$$C(\eta = -\infty) = C_0, \quad C(\eta = \infty) = C^0, \quad \left. \frac{dC}{d\eta} \right|_{-\infty} = \left. \frac{dC}{d\eta} \right|_{\infty} = 0. \quad (20.11)$$

Integrating (20.10) leads to a first-order ordinary differential equation

$$uC - R(C)u^s C + B_1 = D_L \frac{dC}{d\eta}, \quad (20.12)$$

where B_1 is an integration constant.

Let us introduce an auxiliary function (Dou and Jin 1996)

$$S(C) = \int R(C) dC = C + \frac{f(C)}{\phi} + B_2 \quad (20.13)$$

(B_2 is a constant), allowing Eq. 20.12 to be transformed into

$$uC - u^s \left(C + \frac{f(C)}{\phi} \right) + B_1 - B_2 u^s = D_L \frac{dC}{d\eta}. \quad (20.14)$$

Since, in accordance with the initial formulation of the problem (20.11), when $dC/d\eta \rightarrow 0$, the conditions $C \rightarrow C_0$ and $C \rightarrow C^0$ must hold, we come to the following system of equations:

$$uC_0 - u^s \left(C_0 + \frac{f(C_0)}{\phi} \right) + B_1 - B_2 u^s = 0, \quad (20.15a)$$

$$uC^0 - u^s \left(C^0 + \frac{f(C^0)}{\phi} \right) + B_1 - B_2 u^s = 0. \quad (20.15b)$$

Its solution yields

$$u^s = \frac{u}{1 + \frac{f(C_0) - f(C^0)}{\phi(C_0 - C^0)}} = \frac{u}{R} \left(R = 1 + \frac{\Delta f(C)}{\phi \Delta C} = \text{const} \right), \quad (20.16)$$

$$B_1 - B_2 u^s = 0. \quad (20.16a)$$

It can be seen that the displacement of the concentration wave has the constant velocity (20.1), i.e., the motion velocity of the dispersed ($D_L > 0$) stationary front is determined by the same formula as the piston-like displacement velocity (with $D_L = 0$).

Thus, the process is described by an ordinary differential equation

$$D_L \frac{dC}{d\eta} = (u - u^s)C - u^s \frac{f(C)}{\phi}. \quad (20.17)$$

Its integration yields

$$\eta(C) = \eta_0(C) + B_3, \quad (20.18)$$

i.e., an equation describing the profile of a stationary front for solute concentration, where

$$\eta_0(C) = A \frac{R}{R-1} \int \frac{dC}{C - f(C)/\phi(R-1)}, \quad (20.18a)$$

B_3 is integration constant; R is the retardation factor, as in (20.16); $A = \delta_L + D_m/u$ (δ_L is the dispersivity, D_m is the coefficient of pore diffusion).

Because of its equilibrium character, the sorption process is accompanied by the formation of a sorption wave

$$\eta(N) = \eta_0(N) + B_3, \quad (20.19)$$

moving in the direction of flow with the same velocity u^s , allowing us to write the identity (Rachinsky 1964)

$$\eta(C) = \eta(N) = \eta(C + N). \quad (20.20)$$

The equation for the core of solution $\eta_0(N)$ can be obtained, if we consider N as the inverse function to C :

$$N = f(C), \quad C = f^{-1}(N) \equiv F(N). \quad (20.21)$$

Substituting (20.21) into (20.18a) yields

$$\eta_0(N) = A \frac{R}{R-1} \int \frac{F'(N)dN}{F(N) - N/\phi(R-1)}, \quad F'(N) = \frac{dC}{dN}. \quad (20.22)$$

To determine the final solution of the problem, we have to evaluate the integration constant B_3 . With this in view, we use the matter conservation law, assuming that in any moment the amounts (masses) of matter in the system are the same for the piston-like displacement problem (pistone-like displacement, $D_L = 0$) and the problem with a stationary front of dispersion mixing ($D_L > 0$):

$$\phi \int_0^{C_0} x dC + \int_0^{N_0} x dN = (\phi C_0 + N_0) u^s t \quad (20.23)$$

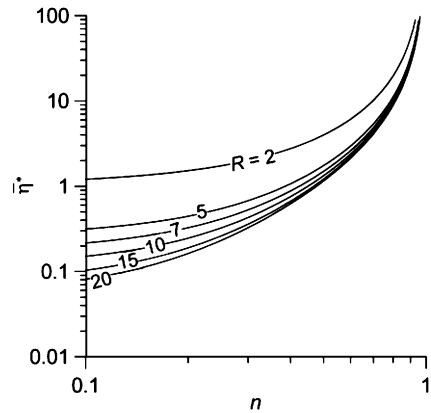
(to simplify the transformations, we assume zero initial conditions, $C^0 = 0$ and $N^0 = 0$). Substituting the current values $x = u^s t + \eta(C)$ and $x = u^s t + \eta(N)$ into the above equality, we obtain

$$\phi \int_0^{C_0} \eta(C) dC + \int_0^{N_0} \eta(N) dN = 0. \quad (20.24)$$

This expression, upon the substitution of functions $\eta(C)$ and $\eta(N)$, allows us to determine the unique constant

$$B_3 = - \frac{\phi \int_0^{C_0} \eta_0(C) dC + \int_0^{N_0} \eta_0(N) dN}{\phi C_0 + N_0} = - \frac{\int_0^1 \eta_0(\bar{C}) d\bar{C} + (R-1) \int_0^1 \eta_0(\bar{N}) d\bar{N}}{R}, \quad (20.25)$$

Fig. 20.1 Plot of function $\bar{\eta}^*(n) = \eta^*/A$ at different values of parameter R



$\bar{C} = N/C_0$, $\bar{N} = N/N_0$. For example, in the case of a Freundlich sorption isotherm, the integration of (20.25) and (20.22) yields

$$\eta_0(\bar{C}) = \frac{AR}{(1-n)(R-1)} \ln(1 - \bar{C}^{1-n}), \quad (20.26a)$$

$$\eta_0(\bar{N}) = \frac{ARn}{(1-n)(R-1)} \ln(1 - \bar{N}^{(1-n)/n}). \quad (20.26b)$$

Substituting (20.26) in (20.25), we find

$$B_3 = \eta^* = -\frac{A}{p} \int_0^1 \ln(1 - y^m) \left(\frac{1}{R-1} + \frac{n^2}{y^m} \right) dy, \quad m = 1 - n \quad (20.27)$$

(see Fig. 20.1). The final solution of the problem can be written as:

$$\bar{C}(\eta) = \left\{ 1 - \exp \left[\frac{(1-n)(R-1)}{AR} (\eta - \eta^*) \right] \right\}^{\frac{1}{1-n}}, \quad \eta \leq \eta^*. \quad (20.28)$$

Equation (20.17) is the Bernoulli differential equation, which for Freundlich sorption isotherm becomes:

$$\frac{d\bar{C}}{d\eta} = \frac{R-1}{AR} (\bar{C} - \bar{C}^n). \quad (20.29)$$

This equation was studied by van der Zee (1990). He found a good approximation of the integration constant for the isotherm under study (van der Zee 1990; Vanderborght et al. 2005),

$$\eta^* = -A \left[1 - \frac{R}{(1-n)(R-1)} \sum_{j=1}^{1/(1-n)} \frac{1}{j} \right], \quad (20.30)$$

valid for the values $n = i/(1+i)$, where i is a positive integer. Clearly, the condition for the applicability of (20.30) is $n > 0.5$. In a more general case, it is practical to use the integral form of (20.27) or plots in Fig. 20.1.

20.1.3 The Influence of Nonlinear Sorption on Advective Transport of a Decayed Component

Neglecting longitudinal dispersion, we write the balance equation in the following generalized form (one-dimensional problem):

$$\phi \frac{\partial C}{\partial t} + \frac{\partial N}{\partial t} + q \frac{\partial C}{\partial x} + \phi \lambda C + \lambda N = 0. \quad (20.31)$$

As can be seen from Eq. 20.31, it is assumed that the transport of unstable component is accompanied by its decay, taking place in both the liquid and solid (adsorbed state) phases; in this formulation of the migration problem, the decay constants (λ) are the same. Its solution reduces to evaluating the displacement velocity of the concentration front $x = x^*(t)$ and finding the equation of concentration function $C = C(x, t)$ in the interval $0 \leq x \leq x^*$. For definiteness sake, we will consider the sorption of the component described by nonlinear Freundlich isotherm (19.2).

First, we solve an auxiliary problem for a stationary concentration distribution ($t \rightarrow \infty$). With the stationarity conditions $\partial C / \partial t = 0$ and $\partial N / \partial t = 0$, Eq. 20.31 becomes

$$\frac{dC}{dx} + \frac{\lambda}{u} C + \frac{\lambda K_F^s}{u \phi} C^n = 0, \quad (20.32)$$

or, for the relative concentration ($\bar{C} = C/C_0$)

$$\frac{d\bar{C}}{dx} + \frac{\lambda}{u} \bar{C} + \frac{\lambda}{u} (R-1) \bar{C}^n = 0, \quad (20.33)$$

where $R = 1 + \frac{K_F C_0^{n-1}}{\phi}$ is the retardation factor. The substitution

$$y = \bar{C}^{1-n} \quad (20.34)$$

allows Eq. 20.33 to be transformed to the linear form

$$y' + ay + b = 0, \quad y' = dy/dx, \quad (20.35)$$

where $a = (1-n) \frac{\lambda}{u}$, $b = (1-n)(R-1) \frac{\lambda}{u}$.

The general solution of the ordinary linear differential Eq. 20.35 is known to have the form (Kamke 1977)

$$y = e^{-ax} \left(A - \int b e^{ax} \right), \quad (20.36)$$

where A is integration constant, which can be found from the condition $\bar{C}(x=0)=1$,

$$A = 1 + \frac{b}{a}. \quad (20.36a)$$

Returning from function y back to the relative concentration $\bar{C}$, with simple algebraic transformations, we obtain the following solution:

$$\bar{C} = e^{-\lambda x/u} \left[1 + (R-1) \left(1 - e^{\lambda(1-n)x/u} \right) \right]^{\frac{1}{1-n}}, \quad (20.37a)$$

or, in the dimensionless form

$$\bar{C} = e^{-\xi} \left[1 + (R-1) \left(1 - e^{(1-n)\xi} \right) \right]^{\frac{1}{1-n}}, \quad (20.37b)$$

where $\xi = \lambda x/u$. It can be readily seen that function $\bar{C} = \bar{C}(x)$ is not monotonous: it decreases for $0 \leq x < x^0$ and increases for $x > x^0$; in point $x = x^0$, $\bar{C} = 0$. Therefore, the solution (20.37) is valid in the domain:

$$x \leq x^0 = \frac{1}{1-n} \frac{u}{\lambda} \ln \left(\frac{R}{R-1} \right), \quad (20.38a)$$

or

$$\xi \leq \xi^0 = \frac{1}{1-n} \ln \left(\frac{R}{R-1} \right). \quad (20.38b)$$

The physical meaning of this inequality is obvious: the *stationary* concentration wave cannot propagate over a distance greater than some critical value x^0 because of the “disappearance” of migrating solute from the system in the process of its irreversible decay. With $n = 1$, the solution (20.37) degenerates into the well-known exponential dependence

$$\bar{C} = e^{-\lambda x R/u} = e^{-\xi R}, \quad (20.39)$$

describing the migration of an unstable component with linear sorption $R = 1 + K_d \rho_b / \phi$ ($K_F = K_d \rho_b$). With $R = 1$, formulas (20.37) yield another well-known limiting solution for the migration of an unstable inert component.

Now we can come to solving the second part of the problem, i.e., the construction of a model for calculating the motion of the leading front of the concentration wave $x^*(t)$. We proceed from the hypothesis (Bosma and van der Zee 1993) that a stationary distribution (20.37) rapidly (theoretically, instantaneously) settles behind its front (at $x < x^*$) and the maximal possible concentration is attained. Now the equation of front motion takes the transcendent form:

$$x^* = \frac{ut}{\langle R(x^*) \rangle}, \quad (20.40)$$

where $\langle R(x^*) \rangle$ is the mean value of the retardation factor over the interval $0 \leq x \leq x^*$,

$$\langle R(x^*) \rangle = \frac{1}{x^*} \int_0^{x^*} R(\xi) d\xi, \quad (20.40a)$$

and, in accordance with the accepted hypothesis, we have for Freundlich isotherm

$$R(\xi) = f[R(C_0^*)] = 1 + \frac{K_F}{\phi} [C_0^*(\xi)]^{n-1}; \quad (20.40b)$$

here, C_0^* is the stationary distribution (20.37): $C_0^* = \bar{C}C_0$. Substituting (20.37) into (20.40b), we obtain:

$$R(\xi) = 1 - \frac{1}{1 - \bar{R} \exp(-a\xi)}, \quad \bar{R} = \frac{R}{R-1}, \quad a = (1-n) \frac{\lambda}{u}. \quad (20.41)$$

Thus,

$$\langle R(x^*) \rangle = \frac{1}{x^*} \int_0^{x^*} \left[1 - \frac{1}{1 - \bar{R} \exp(-a\xi)} \right] d\xi = -\frac{1}{ax^*} \ln \left| 1 - R(1 - e^{-ax^*}) \right|. \quad (20.41a)$$

After substitution of (20.41a) in (20.40) and some additional transformations, we find an explicit expression for coordinate x^* :

$$x^* = x^*(t) = -\frac{u}{(1-n)\lambda} \ln \left(1 - \frac{1}{R} \left(1 - e^{-(1-n)\lambda t} \right) \right); \quad (20.42a)$$

and in a dimensionless form

$$\xi^* = \xi^*(\tau) = -\frac{1}{(1-n)} \ln \left(1 - \frac{1}{R} \left(1 - e^{-(1-n)\tau} \right) \right), \quad \tau = \lambda t. \quad (20.42b)$$

With $t \rightarrow \infty$, we have $x^* = x^0$, i.e., the coordinate x^0 (20.38a) indeed bounds the zone of maximal possible concentration perturbation during the migration in a bed of an unstable component, which is nonlinearly adsorbed by solid/mineral phase. Other well-known limits also follow from the solution (20.42). Thus, with $\lambda t \rightarrow 0$ (migration of a stable component or the initial stages of the process), we have $x^*(t) = ut/R$ ($\xi^*(\tau) = \tau/R$), i.e., the concentration front corresponds to piston-like displacement and its motion is governed by a common kinematic relationship.

Figure 20.2, constructed using the obtained analytical solution (20.37), (20.42), illustrates the main regularities of the process. In particular, the results given above show that the more considerable the nonlinearity of sorption process, the less the velocity of the concentration front, and eventually, the less the propagation of the plume from the pollutant source.

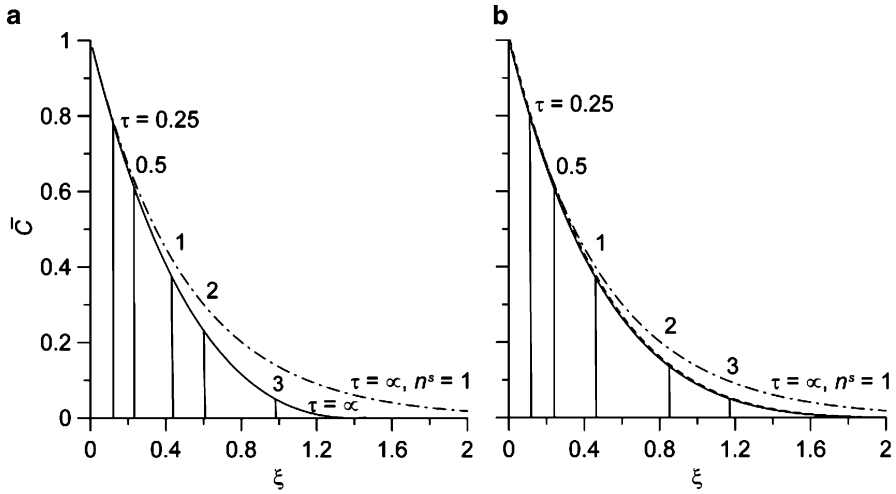


Fig. 20.2 Formation of concentration fronts of an unstable component. (a) $n = 0.5$, (b) $n = 0.7$. The *full lines* are for the analytical solution (20.37), (20.42) for nonlinear sorption; the *dash-and-dot line* is for the limiting solution (20.39) for linear sorption. $R = 2$

The solution of the initial problem in a strict formulation, corresponding to the model

$$[1 + (R - 1)\bar{C}^{n-1}] \frac{\partial \bar{C}}{\partial \tau} + \frac{\partial \bar{C}}{\partial \xi} + \bar{C} + (R - 1)\bar{C}^n = 0, \quad (20.43)$$

$$\bar{C}(0, \tau) = 1, \bar{C}(\xi, 0) = 0, \quad (20.44)$$

has been obtained numerically. The calculation algorithm is based on the solution of a system of ordinary differential equations:

$$\frac{d\tau}{1 + (R - 1)\bar{C}^{n-1}} = \frac{d\xi}{1} = -\frac{d\bar{C}}{(1 + (R - 1)\bar{C}^{n-1})\bar{C}}, \quad (20.45)$$

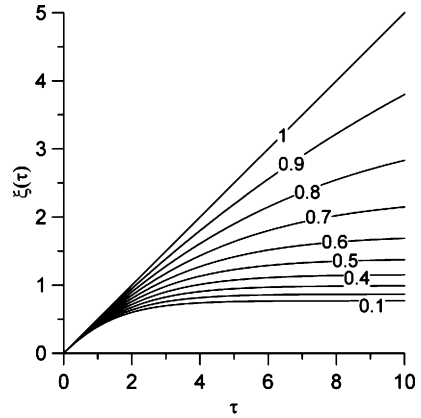
which is equivalent to the system of partial differential equations (20.43), or

$$\frac{d\xi(\tau)}{d\tau} = \frac{1}{1 + (R - 1)\bar{C}^{n-1}}, \quad (20.46a)$$

$$\frac{d\bar{C}(\tau)}{d\tau} = -\bar{C}(\tau). \quad (20.46b)$$

The plot of characteristics constructed in this manner (Fig. 20.3) almost completely (with an error of less than a few tenths of percent) coincides with calculations by (20.42b).

Fig. 20.3 Plot of characteristics at $R = 2$ and different values of n (numbers at curves)



Thus, the analytical model (20.37), (20.42b) gives an accurate description of the migration of an unstable component, i.e., the initial hypothesis that the concentration function is steady behind the pollutant front has proved to be productive, and the method used to average parameter R is correct.

20.1.4 The Influence of Sorption Hysteresis on Concentration Front Displacement

Consider the formation of one-dimensional concentration fields at $D_L = 0$ using simple kinematic and balance relationships. Suppose that the input concentration function is of a square-pulse type (Fig. 20.4a), i.e., a solution containing a stable sorption marker with concentration $C = C_{10}$ enters the bed within a limited time t_s , after which the concentration drops to the initial background level $C = 0$. The sorption and desorption are of equilibrium character and are governed by partial distribution coefficients $K_1 \equiv K_{F1}$ and $K_2 \equiv K_{F2}$ (19.6), respectively.

It is well known (Rachinsky 1964; Charbeneau 1981), that the convexity of desorption isotherm (Eq. 19.7, Fig. 19.1), $N^d(C)$, should lead to “erosion” of the rear desorption front that forms when the polluted zone in the bed is washed by “clear” water (Fig. 20.4b). The appropriate concentration field can be described by the characteristic equation

$$x = \frac{q(t - t_s)}{\phi + dN^d/dC}, \quad (20.47a)$$

which can be written in the following dimensionless form:

$$\bar{x} = \frac{\bar{t} - 1}{1 + n_1 \beta_1 \bar{C}^{n_1 - 1}}, \quad (20.47b)$$

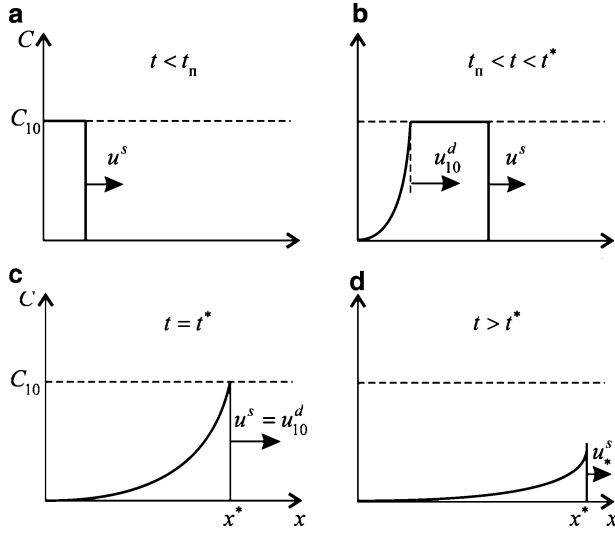


Fig. 20.4 The distribution of adsorbed component in solution in the case of hysteresis equilibrium sorption. (a, b, c, d) Different stages of migration process

where $\bar{x} = x\phi/qt_s$, $\bar{t} = t/t_s$, $\bar{C} = C/C_{10}$, $\beta_1 = fK_1C_{10}^{n_1-1}/\phi \equiv f(R_1 - 1)$, R_1 is a factor of sorption retardation on first-type reactive (sorption) sites, q is Darcy velocity, ϕ is porosity.

The leading sorption front moves with the velocity

$$u^s = \frac{q}{\phi + \Delta N^s / \Delta C} \quad (20.48a)$$

(in this case, $\Delta N^s / \Delta C = N^s / C_{10}$), or in a dimensionless form

$$\bar{u}^s = \frac{1}{1 + \beta_1 + \beta_2} \quad \left(\bar{u}^s = \frac{u^s}{u}, u = \frac{q}{\phi} \right), \quad (20.48b)$$

where $\beta_2 = (1 - f)K_2C_{10}^{n_2-1}/\phi \equiv (1 - f)(R_2 - 1)$, R_2 is the factor of sorption retardation on second-type reactive sites. This velocity is always less than that of high-concentration points (in particular, $\bar{C} = 1$) of the leading desorption front

$$\bar{u}_{10}^d \equiv \bar{u}^d \Big|_{\bar{C}=1} = \frac{d\bar{x}}{d\bar{t}} \Big|_{\bar{C}=1} = \frac{1}{1 + n_1\beta_1} (> \bar{u}^s). \quad (20.49)$$

Therefore, after some time, t^* , the desorption front starts interacting with the sorption front (Fig. 20.4c, d). The superposition of fronts leads to a drop in the concentration on the leading displacement front, resulting, because of the nonlinearity of the process, in a decrease in its migration velocity. The time $\bar{t}^*$ ($\bar{t}^* = t^*/t_s$) can be readily found from the relationship $\bar{u}^s \bar{t}^* = \bar{u}_{10}^d (\bar{t}^* - 1)$:

$$\bar{t}^* = \frac{(1 + \beta_1 + \beta_2)}{(1 - n_1)\beta_1 + \beta_2} = \frac{\bar{f}R_1 + R_2}{\bar{f}(1 - n_1)(R_1 - 1) + (R_2 - 1)}, \quad (20.50a)$$

$\bar{f} = f(1 - f)^{-1}$. This time corresponds to the linear displacement (Fig. 20.4c)

$$\bar{x}^* = \frac{1}{(1 - n_1)\beta_1 + \beta_2} = \frac{1}{\bar{f}(1 - n_1)(R_1 - 1) + (R_2 - 1)}. \quad (20.50b)$$

In the case of superposition of sorption and desorption waves, the migration velocity of the leading front, u_*^s , will be governed by the slower process. In the process of hysteresis sorption with the generalized isotherm (19.7), this is the desorption process. From balance considerations, we have

$$\bar{u}_*^s = \frac{1}{1 + \beta_1 \bar{C}_*^{n_1-1} + \beta_2 / \bar{C}_*} \quad \left(\bar{u}_*^s = \frac{u_*^s}{u} \right). \quad (20.51)$$

The evaluation of current values of concentration $\bar{C}_* = C_*/C_{10}$ requires the use of special numerical iteration techniques.

Figure 20.5 gives the calculated concentration distributions $\bar{C}(\bar{x})$ (starting from the moment of “shock” interaction between the fronts, $\bar{t} \geq \bar{t}^*$) at different values of parameter β_i ($\beta_2 = 0$, $\beta_1 = 1.2$ is the case of reversible sorption, and $\beta_2 = 0.2$, $\beta_1 = 1.0$ is the case of partially irreversible sorption) and at fixed values of the “exponential” constant $n_1 = n_2 (= 0.7)$. With such combination of parameters β_i and n_i , the sorption isotherm remains unchanged for reversible and irreversible processes. It can be clearly seen that the irreversibility of a process facilitates more rapid suppression of the concentration perturbation in the bed.

The other two plots (Fig. 20.6) illustrate the effect of parameter n_1 on the velocity characteristics of the leading sorption front. It can be seen that since the beginning of interaction between desorption and sorption waves, the velocity of component migration at the front of contact between polluted and clear (formation) water steadily decreases (in our example, from $\bar{u}^s = 0.455$ (20.48b) to 0). The rate of decrease in this velocity ($\partial u_*^s / \partial t$) depends on the nonlinearity of the process: the greater the constants n_1 , the more abrupt the front slowdown.

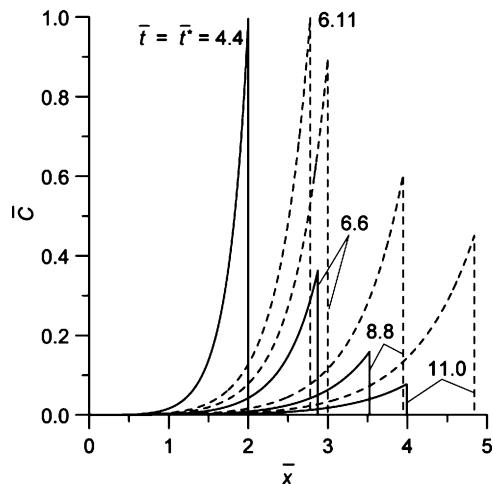


Fig. 20.5 The effect of the irreversibility of the process on the character of concentration distributions. The *full lines* are for irreversible sorption ($\beta_2 = 0.2$, $\beta_1 = 1.0$), the *dashed lines* are for reversible equilibrium sorption ($\beta_2 = 0$, $\beta_1 = 1.2$); $C_{10} = 1$ and $n_1 = 0.7$

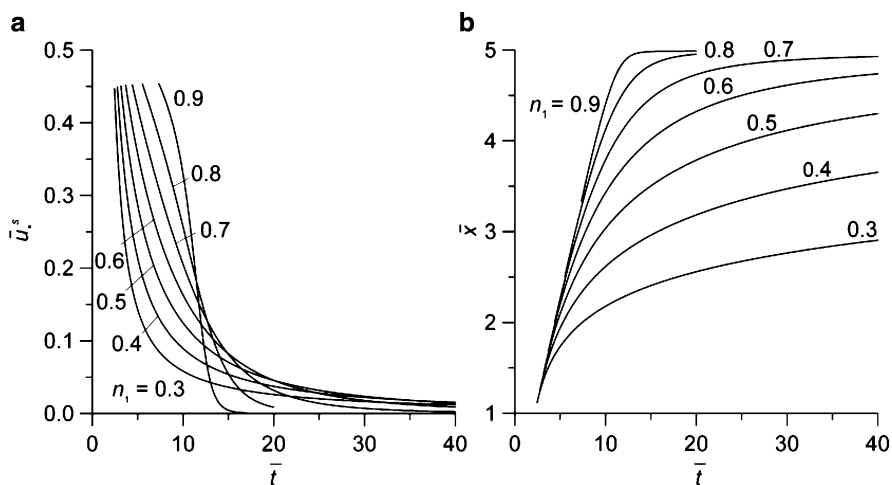


Fig. 20.6 The effect of parameter n_1 on the velocity of the leading front of concentration wave. (a) $\bar{u}_s^s - \bar{t}$, (b) $-\bar{x} - \bar{t}$ (characteristic curves). $C_{10} = 1$, $\beta_1 = 1.0$, $\beta_2 = 0.2$

These calculations show that the nonlinearity of the sorption process described by a linear model should lead to an increase over time in the calculated (effective) values of the sorption distribution coefficient, as can be seen from the analysis of field data collected in groundwater pollution areas (Kasteel et al. 2002; Mojid and Vereecken 2005).

A special case is the linear irreversible sorption ($n_1 = n_2 = 1$), which yields a piston-like desorption front. This front, moving with a velocity equal to the actual flow velocity, tends to catch up the sorption front, resulting in a contraction of the zone of polluted water. At some moment, t^* , the fronts merge (u^s instantaneously drops to the value $u^s = u_*^s = 0$): at this moment, all polluting components will pass from liquid to solid phase, i.e., because of the hysteresis of sorption process and its irreversibility, groundwater quality will be restored in the previously polluted zones. The time t^* can be readily found from simple kinematic relationships or directly from the formula

$$\bar{t}^* = \frac{t^*}{t_s} = 1 + f \frac{R_1}{R_2}, \quad (20.52)$$

where $R_i = 1 + K_i/\phi$ ($i = 1, 2$; ϕ is the porosity).

Thus, notwithstanding the presence of pollutants in the bed, groundwater quality can remain high over infinitely long time both within the local area of bed pollution (were all components are accumulated by solid phase) and further downstream. The volumetric concentration, N^0 , of the pollutant in the solid phase can be calculated as

$$N^0 = (1 - f) K_2 C_{10}. \quad (20.53)$$

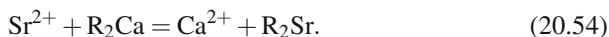
However, under real conditions, a rapid drop to the background concentrations can be hampered by desorption kinetics. Mathematical modeling can be used to study the role of this mechanism in mass transport (see Sect. 20.2.3).

20.1.5 *On Incorporation of a Geochemical Phenomenon into a Radionuclide Transport Model*

Some recent studies are focused on the analysis of the mechanisms that maintain the “fast” (with actual water velocity) transport of chemical components that are conventionally regarded in hydrogeochemistry as well absorbable. The greatest attention is paid to the category of highly toxic migrants, primarily, radionuclides. The rapid transport of components can be due to a number of factors, including complex formation; adsorption on colloidal particles (Chaps. 24 and 25); the formation of ion exchange waves and dissolution waves, induced by the flow (Sects. 15.3.2 and 23.1.2.1); and the existence of prevailing migration paths. In this section, we will analyze the fast transport of a radionuclide due to the presence of Clarke concentration of its stable isotope in groundwater and the rocks in contact with it.

20.1.5.1 A Two-Component (Sr–Ca) System

This is the simplest case to consider the influence of the presence of a stable form of some component on the migration rate of some its radioactive isotope. For the sake of definiteness, we assume that the factor governing the migration rate of the strontium-containing solution is the ion exchange in the system:



Next, we assume that radioactive strontium (Sr-90) accounts for a small part β of the total bulk strontium concentration C_1 in the solution entering the bed (aquifer), i.e.

$$C_1^s = (1 - \beta)C_1, \quad C_1^* = \beta C_1, \quad (20.55)$$

where C_1^s and C_1^* are the concentrations of the stable and radioactive isotopes, such that $C_1^s + C_1^* = C_1$. The physicochemical parameters of sorption interactions for stable and radioactive forms of strontium are assumed to be equivalent.

The isothermal representation of the exchange reaction is convenient to use. Thus, the application to Eq. 20.54 of the mass action law in the form

$$K_{12} = \frac{C_2 N_1}{C_1 N_2}, \quad (20.56a)$$

supplemented with equations of solution electric neutrality and the invariability of the exchange complex capacity

$$C_1 + C_2 = C_0, \quad N_1 + N_2 = N_v \quad (20.56b)$$

yields isotherms of the form

$$N_1 = \frac{K_{12}N_vC_1}{C_0 + (K_{12} - 1)C_1}, \quad N_2 = \frac{N_vC_2}{K_{12}C_0 + (1 - K_{12})C_2}; \quad (20.57)$$

here K_{12} is the selectivity coefficient; C_i and N_i are cation concentrations in the liquid phase and the sorption complex, $i = 1, 2$ ($i = 1$ refers to Sr, $i = 2$ refers to Ca); C_0 is the concentration of anions; N_v is the exchange capacity; all concentrations have the dimension of mol/L.

The displacement is assumed to be piston-like in the sense that a sharp interface exists between the displacing fluid, which inherits the composition of the inflow solution

$$C_0 = C_{00}, \quad C_1 = C_{10}, \quad C_2 = C_{20} \quad (20.58a)$$

(boundary condition, $t > 0$, $x = 0$), and the displaced fluid, reflecting the composition of the formation solution

$$C_0 = C_0^0, \quad C_1 = C_1^0, \quad C_2 = C_2^0, \quad N_1 = N_1^0, \quad N_2 = N_2^0 \quad (20.58b)$$

(initial condition, $t = 0$, $x > 0$).

The difference between the concentrations of ions in the displacing and displaced solutions, in particular, $C_0^0 \neq C_{00}$, leads to a disturbance in the physicochemical equilibrium in the mobile hydrochemical system. Two concentration waves (zones) form in this system (Fig. 20.7): (1) the boundary and (2) the leading zone. On the moving boundary between these waves, part of cations is either adsorbed or desorbed. This process proceeds with the rate that ensures the attainment of equilibrium concentrations C_1^p and C_2^p within the leading zone:

$$C_1^p + C_2^p = C_{00}. \quad (20.59)$$

For the solution to remain electrically neutral, the displaced and displacing cations (their concentrations are C_1^p and C_2^p , respectively) must move with the same velocity as anions, i.e., with the actual velocity of water particles. This is possible only if no sorption–desorption of cations takes place under given conditions, i.e., when the following conditions are satisfied:

$$N_1(C_1^p, C_{00}) = N_1(C_1^0, C_0^0), \quad (20.60a)$$

$$N_2(C_2^p, C_{00}) = N_2(C_2^0, C_0^0). \quad (20.60b)$$

From here we find for the two-cation system in question

$$C_1^p = \frac{C_{00}}{C_0^0} C_1^0, \quad C_2^p = \frac{C_{00}}{C_0^0} C_2^0 \quad (20.61)$$

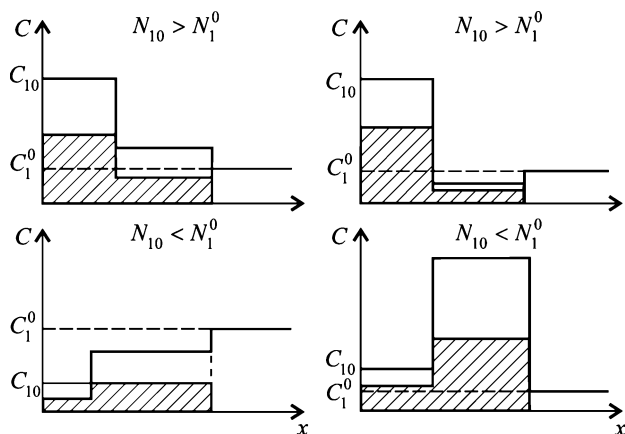


Fig. 20.7 The behavior of concentration fronts at different directions of ion exchange process. The *full line* is the concentration of total strontium (C_1), and the *dashed part* of the plot is the concentration of Sr-90

(it can be readily seen that $C_1^p + C_2^p = C_{00}$). Within the near-boundary concentration wave, the concentrations C_{10} and C_{20} correspond to new values N_{10} and N_{20} , which differ from N_1^0 and N_2^0 and depend on the selectivity coefficient K_{12} and the exchange capacity $N_v (= N_{10} + N_{20})$.

Next, let us consider the behavior of Sr-90 in the composition of strontium–calcium solution entering the bed. With this in view, we write the basic balance equations for the two identified hydrochemical zones:

the boundary zone:

$$C_{10}^* + C_{10}^s = \beta C_{10} + (1 - \beta) C_{10} = C_{10}, \quad (20.62a)$$

$$N_{10}^* + N_{10}^s = N_{10}, \quad (20.62b)$$

$$\frac{N_{10}^*}{N_{10}^s} = \frac{C_{10}^*}{C_{10}^s} = \frac{\beta}{1 - \beta}; \quad (20.62c)$$

the leading zone:

$$(C_1^*)^p + (C_1^s)^p = C_1^p, \quad (20.63a)$$

$$(N_1^*)^p + (N_1^s)^p = N_1^p, \quad (20.63b)$$

$$\frac{(N_1^*)^p}{(N_1^s)^p} = \frac{(C_1^*)^p}{(C_1^s)^p}, \quad (20.63c)$$

and the equation determining the condition of equality of the migration velocities of radioactive and stable strontium at the contact between the two zones:

$$\frac{N_{10}^s - (N_1^s)^p}{C_{10}^s - (C_1^s)^p} = \frac{N_{10}^* - (N_1^*)^p}{(C_{10}^*) - (C_1^*)^p}. \quad (20.64)$$

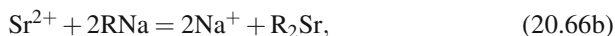
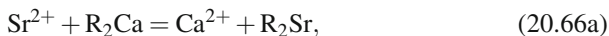
Solving this system of equations, we find that the concentration of Sr-90 within the leading zone (wave) will be determined by the relationship

$$(C_1^*)^p = \beta C_1^p, \text{ accordingly, } (C_1^s)^p = (1 - \beta)C_1^p. \quad (20.65)$$

For the two-component system in question, C_1^p is determined by (20.61). Thus, the presence of stable strontium in groundwater in arbitrarily low concentrations always causes the appearance of Sr-90 near the front of the leading wave, moving with the velocity equal to that of water particles, and, as it follows from (20.65), the concentration $(C_1^*)^p$ can exceed the concentration of Sr-90 in the inflow solution βC_{10} .

20.1.5.2 A Three-Component (Sr–Ca–Na) System

The inclusion into consideration of ions of alkaline metal Na^+ shifts the system Sr(Sr-90) - Ca - Na to the “typical” natural system. This system can be described by the following equilibrium state:



The selectivity coefficients of reactions (20.66) are determined by the equalities

$$K_{12} = \frac{C_2 N_1}{C_1 N_2}, \quad K_{13} = \frac{C_3^2 N_1}{C_1 N_3^2}, \quad K_{23} = \frac{C_3^2 N_2}{C_2 N_3^2}, \quad \frac{K_{13}}{K_{23}} = K_{12}; \quad (20.66d)$$

subscripts 1, 2, and 3 refer to ions of strontium, calcium, and sodium, respectively.

Proceeding from the concept of zonal regime of mass transport, which involves the presence of a leading $(C_1^p, N_i^p, i = 1, 2, 3)$ and near-boundary (C_{i0}, N_{i0}) concentration waves with an abrupt interface, by analogy with the analysis given above, we can write:

$$2C_1^p + 2C_2^p + C_3^p = C_{00}, \quad (20.67a)$$

$$2N_1^p + 2N_2^p + N_3^p = N_v, \quad (20.67b)$$

$$2N_{10} + 2N_{20} + N_{30} = N_v, \quad (20.67c)$$

$$\frac{N_1^p}{N_2^p} = K_{12} \frac{C_1^0}{C_2^0}, \quad (20.67d)$$

$$\frac{N_1^p}{(N_3^p)^2} = K_{13} \frac{C_1^0}{(C_3^0)^2}, \quad (20.67e)$$

$$\frac{N_1^p}{N_2^p} = K_{12} \frac{C_1^p}{C_2^p}, \quad (20.67f)$$

$$\frac{N_1^p}{(N_3^p)^2} = K_{13} \frac{C_1^p}{(C_3^p)^2}, \quad (20.67g)$$

$$\frac{N_{20}}{(N_{30})^2} = \frac{K_{13}}{K_{12}} \frac{C_{20}}{(C_{30})^2}, \quad (20.67h)$$

The leading front (the interface between waters with concentrations C_i^p , N_i^p and C_i^0 , N_i^0) moves with the velocity equal to the actual migration velocity of inert components (anions): $u = q/\phi$. The displacement velocity of the interface between waters with concentrations C_{i0} , N_{i0} and C_i^p , N_i^p , is

$$u = \frac{v}{\phi + \Delta\phi}, \quad (20.68)$$

where

$$\Delta\phi = \frac{N_{i0} - N_i^p}{C_{i0} - C_i^p}, \quad i = 1, 2, 3, \quad (20.69a)$$

or

$$\frac{N_{10} - N_1^p}{C_{10} - C_1^p} = \frac{N_{20} - N_2^p}{C_{20} - C_2^p}, \quad \frac{N_{30} - N_3^p}{C_{30} - C_3^p} = \frac{N_{20} - N_2^p}{C_{20} - C_2^p}. \quad (20.69b)$$

The latter condition is known as an analytical representation of the “principle of coherence”, according to which all cations on the boundary between the leading and near-boundary concentration waves must move with the same rate, governed by the value of additional porosity (storage capacity) $\Delta\phi$. The latter is true for convex isotherms of exchange.

Thus, we come to a system comprising nine equations (20.67)–(20.69b) with nine unknown variables C_i^p , N_i^p and N_{i0} . Its solution can be obtained by iteration methods with the use of specialized software packages.

Let us consider the results of calculations carried out with the following initial conditions

$$C_1^0 = 0.01, \quad C_2^0 = 5.0, \quad C_3^0 = 1.0, \quad N_v = 100 \quad (K_{12} = 2, \quad K_{13} = 4)$$

and boundary conditions

$$C_{10} = 0.02, \quad C_{20} = 1.0, \quad C_{30} = 5 - 300 \quad (C_{00} = 7.04 - 302.4)$$

(all concentrations are given in millimol per liter, mmol/L).

To simplify the analysis, the boundary concentrations of ions of strontium and calcium were fixed and the concentration of sodium ions varied within a wide range. The presented results (Table 20.1) suggest the following conclusions.

1. The ratios between equilibrium concentrations C_i^p/C_i^0 can be different (>1 or <1), depending on sodium concentration in the displacing solution.

Table 20.1 Results of test problem solution

C_{00}^a	C_{30}	Cation	N_{i0}	C_i^p	N_i^p	$\frac{C_i^p}{C_i^0}$	$\frac{N_i^p}{N_i^0}$	$\frac{C_{00}}{C_0^0}$	$\Delta\phi$
7.04	5	Sr	0.26	0.006	0.19	0.62	0.73	0.639	4.7
		Ca	38.74	3.12	48.7	0.62	1.26		
		Na	22.00	0.79	2.21	0.79	0.10		
12.04	10	Sr	0.23	0.011	0.19	1.10	0.83	1.093	4.1
		Ca	30.31	5.49	48.7	1.10	1.61		
		Na	38.92	1.05	2.21	1.05	0.057		
102.04	100	Sr	0.12	0.099	0.19	9.90	1.58	9.260	0.97
		Ca	1.85	49.35	48.7	9.87	26.3		
		Na	96.1	3.14	2.21	3.14	0.02		
302.04	300	Sr	0.10	0.30	0.19	30.0	1.90	27.41	0.33
		Ca	0.22	148	48.7	29.6	221		
		Na	99.4	5.44	2.21	5.44	0.02		

^aThe concentrations are given in mmol/L.

2. When the concentration of sodium ions is low, adsorption of strontium from solution takes place; therefore $\tilde{N}_i^p < C_i^0$ or $C_i^p < C_{i0}$.
3. When the concentration of sodium ions is high, desorption of natural strontium takes place and these ions, along with calcium cations, form a high-concentration wave ($\tilde{N}_{i,2}^p \gg C_{10,20}$). Such behavior of the system is often recorded in real groundwater pollution areas by high-concentration sodium solutions (Rumynin et al. 2005; see also 15.3.2).
4. The concentration of radioactive strontium within the leading concentration wave is determined by (20.61), where parameter β is the relative concentration of the isotope in the initial solution.
5. The additional sorption capacity $\Delta\phi$ in the general case depends on the composition of the displacing solution (other conditions being the same). An increase in the concentrations of sodium ions and water salinity is accompanied by a drop in $\Delta\phi$. When C_{00} is high, we obtain $\Delta\phi \approx N_v/C_{00}$; therefore, this characteristic is practically independent of the values of K_{12} , K_{13} and concentrations C_i^0 and C_{i0} .

20.2 Nonequilibrium Sorption

20.2.1 A Fundamental Solution for Linear Sorption

The system of equations of the form

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + \frac{1}{\phi} \frac{\partial N}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2}, \quad (20.70)$$

$$\frac{\partial N}{\partial t} = \alpha[f(C) - N], \quad (20.70a)$$

which describes nonequilibrium linear sorption (19.12) in the case of $f(C) = KC$ ($K = K_d \rho_b$, α is the first-order rate constant $[T^{-1}]$) is the focus of many studies.

A fundamental solution is the particular solution of the problem (20.70), (20.70a), describing the piston-like (frontal) displacement of solution in porous medium ($D_L = 0$). In this case, analysis of the process in the moving coordinate system (see Eqs. 1.93a, where the independent variables x and t change places)

$$t' = t - x/u, x' = x \quad (20.71)$$

allows the system of equations (20.70), (20.70a) to be transformed into the dimensionless form:

$$-\frac{\partial \bar{C}}{\partial \eta} = \bar{C} - \bar{N}, \quad (20.72)$$

$$\frac{\partial \bar{N}}{\partial \tau} = \bar{C} - \bar{N}, \quad (20.72a)$$

where $\bar{C} = C/C_0$; $\bar{N} = N/KC_0$; $\eta = \alpha Kx/\phi u = \alpha x(R-1)/u$; $\tau = \alpha(t - x/u)$; R is the sorption retardation factor (20.3a); C_0 is the boundary concentration.

The system (20.72)–(20.72a) satisfies the conditions (Schumann 1929; Furnas 1930):

$$\bar{C} = (U + V) \exp(-\eta - \tau), \quad (20.73)$$

$$\bar{N} = (U - V) \exp(-\eta - \tau), \quad (20.74)$$

with

$$V = \frac{1}{2} I_0(2\sqrt{\eta\tau}), \quad (20.75)$$

where $I_0(\cdot)$ is a modified zero-order Bessel function of the first kind. From here we have

$$\bar{C} - \bar{N} = 2V \exp(-\eta - \tau) = I_0(2\sqrt{\eta\tau}) \exp(-\eta - \tau). \quad (20.76)$$

The substitution of the latter equation into (20.72a) and its integration within the limits $[1, \bar{C}]$ and $[0, \eta]$ (zero initial conditions) leads to the solution:

$$\bar{C}(\eta, \tau) = 1 - e^{-\tau} \int_0^\eta e^{-\lambda} I_0(2\sqrt{\lambda\tau}) d\lambda = J(\eta, \tau), \quad (20.77)$$

valid for a step input of concentration. $J(\eta, \tau)$ is the Goldstein function (Sect. 6.1.3.3). Function $J(\eta, \tau)$ was tabulated, and its plots (see, e.g., Fig. 6.3) can be found in numerous publications. Obviously, Eqs. 20.72, 20.72a along with their boundary conditions can be solved using the Laplace transform methods (Sect. 6.1.3.3).

Analysis of solution (20.77) shows that, notwithstanding the absence of hydrodynamic dispersion effects, the transport front will be smoothed as can be seen in indicator plots from gradual decrease in the concentration from $\bar{C} = 1$ to $\bar{C} = 0$ along

the flow. Such shape of the plot is due to the kinetics of the sorption process, whose rate is different in different points of the replacement front. When $t > 10/\alpha$, the solution acquires the asymptotic form close to the solution of one-dimensional microdispersion equation (1.104), when the parameters u and D_L are replaced by the effective coefficients:

$$u_e = \frac{u}{R}, \quad D_e^k = \frac{(1-R)}{\alpha} u_e^2. \quad (20.78)$$

A large number of publications is devoted to solving the system of Eqs. 20.70, 20.70a, supplemented by boundary conditions and, in a complete formulation, with allowance made for the hydrodynamic dispersion of the sorbed component (Lapidus and Amundson 1952; Ogata 1964; Lindstrom and Stone 1974; De Smedt, Wierenga 1979; Davis et al. 2000). Operator methods (Laplace and Fourier transforms) were preferred.

Since the sorption process is considered with the storage capacity assumed lumped, its description can be based on generalized solutions obtained by integral convolution (6.49a), (6.52a) and (6.50). In these solutions, coefficients are changed in the following manner

$$\alpha_m \rightarrow \alpha, \quad \sigma \rightarrow K/\phi = R - 1. \quad (20.79)$$

The calculated curves in Fig. 20.8 illustrate the character of the output concentration function under joint effect of sorption kinetics and hydrodynamic dispersion for a pulse input signal. It can be easily seen that the combined effect of sorption kinetics and hydrodynamic dispersion causes earlier appearance of peak concentration values as compared with the case of piston-like displacement of a component subject to equilibrium sorption ($\bar{D} = 0$, $\alpha \rightarrow \infty$), when $\tau_{\max} = \eta R$. Note also that $\eta/\bar{D} = ux/D_L = \text{Pe}(\eta = \alpha x/u$, $\bar{D} = \alpha D_L/u^2)$.

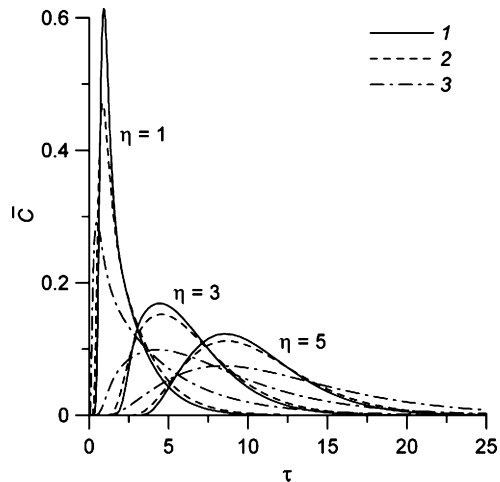


Fig. 20.8 Plot of solution (6.50), describing nonequilibrium linear sorption. $\bar{D}$: 1 – 0.05, 2 – 0.1, 3 – 0.5; $\sigma = 1$ ($R = 2$)

The consideration of long-term asymptotic transport regimes (approximately at $\tau > 10$), described by the model (20.70), (20.70a), also allows combining the dispersion factors of different nature in a generalized factor

$$D_{Le} = D_e^k + D_h + D_m. \quad (20.80)$$

Formula (20.80) can also be represented as:

$$D_{Le} = Au, A = \frac{(R-1)u}{\alpha R^2} + \delta_L + \frac{D_m}{u}, R = 1 + K/\phi, \quad (20.81)$$

where A is the macrodispersivity coefficient for kinetic sorption, R is the retardation factor at linear sorption. The latter relationships can be of use for the subsequent analysis. Thus, the sorption kinetics in homogeneous porous sediments can have more significant effect than the microdispersion. This is true when $q/\alpha K \delta_L > 0.1$.

Special attention should be paid to the migration models that take into account the kinetics of sorption processes described in the static case by nonlinear isotherms. As it is shown below, partial solutions of the appropriate boundary problem can be obtained in the form of a propagating (“advancing”) wave.

20.2.2 Asymptotic Solution of the Problem of Nonlinear Sorption Kinetics

By analogy with the hydrodispersion process (see Sect. 20.1.2), we assume that nonlinear sorption hampers the kinetic erosion of the front, resulting in the formation of a steady concentration wave whose all points move with a constant velocity u^s (Eq. 20.16, *asymptotic* regime). Now the process can be considered in the moving coordinate system (20.8), and transformations (20.9) allow the system of Eqs. 20.70, 20.70a to be converted into

$$-u^s \frac{dC}{d\eta} + u \frac{dC}{d\eta} - D_L \frac{d^2C}{d\eta^2} - \frac{u^s}{\phi} \frac{dN}{d\eta}, \quad (20.82)$$

$$-u^s \frac{dN}{d\eta} = \alpha[f(C) - N]. \quad (20.82a)$$

We integrate Eq. 20.82 from $\eta = -\infty$ ($C = C_0$, $dN/d\eta = 0$) to η (C , $dN/d\eta$), replacing the function N by the expression

$$N = \frac{u^s}{\alpha} \frac{dN}{d\eta} + f(C), \quad (20.83)$$

following from (20.82a), and taking into account

$$\frac{u^s}{u} = \frac{1}{R} = \frac{1}{1 + \Delta f(C)/\phi \Delta C}. \quad (20.83a)$$

The result is the equation

$$-(R-1)(C-C_0) + \frac{D_L R}{u} \frac{dC}{d\eta} + \frac{1}{\phi} [f(C) - f(C_0)] + \frac{u^s}{R \alpha \phi} \frac{dN}{d\eta} = 0. \quad (20.84)$$

Substituting the derivative $dN/d\eta$, determined from (20.82), yields (van der Zee 1990):

$$\frac{D_L}{\alpha} \frac{d^2 C}{d\eta^2} - \left[\frac{D_L R}{u} + \frac{(R-1)}{\alpha R} u \right] \frac{dC}{d\eta} = -(R-1)(C-C_0) + \frac{1}{\phi} [f(C) - f(C_0)]. \quad (20.85)$$

For the further analysis, we assume that (1) the contribution of the second derivative to Eq. 20.84 is negligible, (2) sorption is described by Freundlich isotherm with zero initial conditions $C(\eta = \infty) = 0$, such that

$$R = 1 + K_F C_0^{n-1} / \phi. \quad (20.85a)$$

In this case, we come to an ordinary differential equation similar to (20.17), whose integration yields (20.18) at (20.18a). However, parameter A in the problem under consideration is determined from the relationship

$$A = \delta_L + \frac{D_m}{u} + \frac{(R-1)u}{\alpha R^2}, \quad (20.86)$$

which formally corresponds to the earlier obtained relationship (20.81), describing an asymptotic transport regime under linear kinetic sorption. The difference consists in the form of representation of the retardation factor R (see (20.81) and (20.85a)). Thus, the solution of the problem can be represented in the form of a traveling wave (20.28) with η^* , defined by (20.27), considering (20.86).

Analysis of the structure of expression (20.86) suggests that the experimental studying (either in the laboratory or in the field) of a process proceeding in asymptotic regime will hardly allow one to obtain separate estimates of parameters governing hydrodynamic dispersion and sorption kinetics. It should be expected that the indicator curves will have the same shape at different combinations of parameters δ_L and α yielding the same values of coefficient A (20.86). Therefore, experimental studies of the process should be aimed at a “preasymptotic” migration regime (Simon et al. 1997).

In conclusion, we note that a simplification of the original Eq. 20.85 by excluding from it the second derivative does not cause considerable errors in the description of the process based on the solution (20.28). This conclusion follows from the comparison of this solution with the complete solution of the problem $\left(\frac{D_L}{\alpha} \frac{d^2 C}{d\eta^2} \neq 0 \right)$, obtained for the approximation of a nonlinear isotherm by a piece-wise homogeneous function $N(C)$ (Simon et al. 1997).

20.2.3 A Numerical Model of an Adsorbable Component Transport in Porous Media with Discrete Sorption Sites

A one-dimensional two-site nonequilibrium transport model has been developed to account for the sorption–desorption processes occurring in porous media. The model considers sorption sites exhibiting different energy of sorption, requiring different sets of sorption parameters. First-order reversible kinetic reaction for Freundlich isotherm is a basic sorption process that is included in the algorithm of a numerical simulator. Specifying different values for kinetic and equilibrium parameters at sorption and desorption stages of the process, one may model hysteresis in adsorption.

The general equation of one-dimensional advection–dispersion transport of a component that can be adsorbed at reactive sites of two types (see Sect. 19.2.2) has the form

$$\phi \frac{\partial C}{\partial t} + f \frac{\partial N_1}{\partial t} + (1-f) \frac{\partial N_2}{\partial t} + q \frac{\partial C}{\partial x} = \phi D_L \frac{\partial^2 C}{\partial x^2}, \quad (20.87)$$

where C is the component's concentration in solution, N_i is its concentration in solid phase on the sites of the i th type, f is the mass fraction of the first-type sites, ϕ is the porosity, q is the specific discharge velocity, D_L is the longitudinal dispersion coefficient.

Depending on the direction of the process (sorption or desorption), the transport Eq. 20.87 is supplemented by kinetic Eqs. 19.13a or 19.13b. The system of Eqs. 20.87, 19.13 can be represented in the generalized dimensional form:

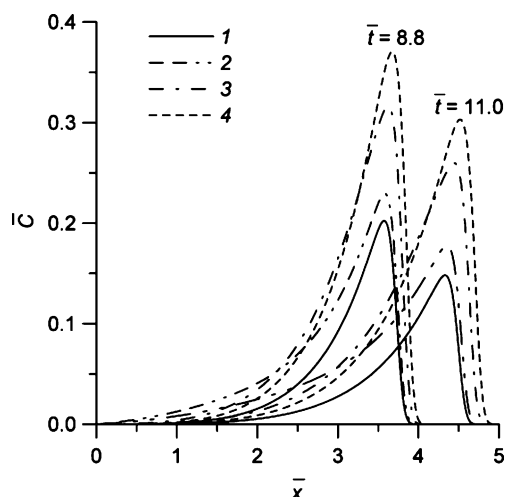
$$\begin{aligned} \frac{\partial \bar{C}}{\partial \bar{t}} + \beta_1 \frac{\partial \bar{N}_1^{s/d}}{\partial \bar{t}} + \beta_2 \frac{\partial \bar{N}_2^{s/d}}{\partial \bar{t}} + \frac{\partial \bar{C}}{\partial \bar{x}} &= \bar{D}_L \frac{\partial^2 \bar{C}}{\partial \bar{x}^2}, \\ f \frac{\partial \bar{N}_1^{s/d}}{\partial \bar{t}} &= \bar{\alpha}_1^{s/d} (\bar{C}^{n_1^{s/d}} - \bar{N}_1^{s/d}), \\ (1-f) \frac{\partial \bar{N}_2^{s/d}}{\partial \bar{t}} &= \bar{\alpha}_2^{s/d} (\bar{C}^{n_2^{s/d}} - \bar{N}_2^{s/d}); \end{aligned} \quad (20.88)$$

here, $\bar{x} = \frac{x}{ut_s}$, $\bar{t} = \frac{t}{t_s}$, $u = q/\phi$, $\bar{C} = \frac{C}{C_{10}}$, $\bar{N}_i^{s/d} = \frac{N_i^{s/d}}{K_i C_{10}^{n_i^{s/d}}}$, $\beta_1 = fK_1 C_{10}^{n_1^{s/d}-1}/\phi$, $\beta_2 =$

$(1-f)K_2 C_{10}^{n_2^{s/d}-1}/\phi$, $\bar{\alpha}_{1,2}^{s/d} = \alpha_{1,2}^{s/d} t_s$, $\bar{D}_L = \frac{D_L}{u^2 t_s}$. It can be seen that this problem formulation takes into account possible differences between parameter values at the sorption (s) and desorption (d) stages of the process. The system of Eq. 20.88 is solved by numerical methods (a numerical simulator, NODEK2t, designed by P.K. Konosavsky).

A series of model experiments was carried out to assess the role of adsorption kinetics from the second-type sites (Fig. 20.9). The sorption was assumed equilibrium ($\alpha_{1,2}^s \rightarrow \infty$); the same assumption was made for the desorption of the component

Fig. 20.9 The effect of desorption kinetics on the concentration distributions $\bar{C}(\bar{x})$. (1) $\bar{\alpha}_2^d = 0.00001$, (2) 0.1, (3) 1.0, (4) 50.0. $\beta_1 = 1$, $\beta_2 = 0.2$, $n = n_2^s = n_1^d = n_2^d = 0.7$, $\bar{D}_L = 10^{-5}$, $f = 0.5$, $C_{10} = 1.0$



from first-type reactive sites ($\alpha_1^d \rightarrow \infty$). In the limiting case ($\alpha_2^d \rightarrow 0$ – a case of irreversible sorption on second-type sites and $\alpha_2^d \rightarrow \infty$ – completely reversible sorption on this type of sites) the results are qualitatively similar to those obtained before in an analytical model (see Sect. 20.1.4): the irreversibility of the process slows down the leading front of the concentration wave and reduces the peak concentration values. Moreover, the calculations showed that, under the assumptions made, the effect of sorption irreversibility is quite appreciable at $\bar{\alpha}_2^d = \alpha_2^d t_s < 0.1$.

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Part VIII

Experimental and Modeling Study of Sorption–Desorption Processes

Recent research findings strongly suggest that the subsurface radionuclide transport is often accompanied by nonideal (anomalous) phenomena caused by (a) adsorption hysteresis facilitated, in particular, by irreversible uptake of radionuclides by a specific group of minerals in the rock matrix or by secondary geochemical alteration of the minerals, (b) deterministic and stochastic heterogeneity of the geological strata resulting in preferential flow paths of the radioactive component, and (c) colloid-facilitated transport. In particular, nonideal radionuclide transport behavior was observed during investigations that have been conducted at several sites associated with near-surface and subsurface radioactive waste (RW) disposal and supervised by RosAtom, the State Nuclear Energy Corporation, Russian Federation.

Two such disposal sites are located within the Northwestern Center of Nuclear Energy (NWCNE), near St. Petersburg: (a) a solid RW disposal site (the so-called *Radon site*), which is used as the northwestern regional surface repository; and (b) an Engineered or Designed Underground Repository (*EUR site*) in the Vendian clay (a regional aquitard) for low- and intermediate-level RW storage and isolation. Two other sites are associated with deep-well injection repositories, operated by the Siberian Chemical Plant and the Siberian Mining-and-Chemical Plant, the *Tomsk-7 site* and *Krasnoyarsk-26 site*, located in Western Siberia. The latter site is associated with a surface reservoir, Lake Karachai, which has been used over a long period for the disposal of liquid RW by the Mayak Production Association (the *Lake Karachai site*), South Ural.

Radioactive wastes contain various long-lived decay products. The most dangerous radionuclides are fission products (such as Sr-90, Cs-137), activated corrosion products (such as Co-60), and actinides (such as Pu-239, Am-241). To evaluate radionuclide behavior in the subsurface environment, sorption and desorption kinetics and equilibrium were measured in batch, diffusion, and column (dynamic) experiments. Rock samples of both sedimentary (unconsolidated and consolidated) and crystalline/fractured types were selected from the radioactively contaminated site (see Table). Core samples of the sandy sediment (the Radon site) were also taken from boreholes to study the spatial variability of the adsorption and desorption constants based on variogram analysis.

Table Summary of the experimental setup: samples, solutions, temperature–pressure, and experimental conditions

RW disposal site	Type of rock	Radionuclides	Solutions	Temperature–pressure	Sample conditioning	Book's section
Radon	Sedimentary: weakly consolidated sandstone	^{90}Sr , ^{137}Cs , ^{60}Co	SGW ^a	Room	Conditioned	21.3–21.4
EUR	Sedimentary: clay	^{90}Sr , ^{36}Cl , ^{60}Co , ^{239}Pu	SGW, SrCl_2	Room	Conditioned	22.6–22.7
Tomsk-7	Sedimentary: clayey sand	^{90}Sr , ^{137}Cs	SGW, NaNO_3	Room, elevated T–P	Conditioned, unconditioned	23.1
Krasnoyarsk-26	Sedimentary: clayey sand	^{90}Sr , ^{137}Cs , ^{239}Pu , ^{241}Am	NaOH + NaNO_3	Room, elevated T–P	Conditioned, unconditioned	23.2
Lake Karachai	Crystalline: tuffs, tuff-and-lava	^{90}Sr	SGW, NaNO_3	Room	Unconditioned	23.3

^a SGW synthesized groundwater

The purpose of this study is to quantitatively evaluate the adsorption-related reactions with respect to natural attenuation, sorption and desorption kinetics and equilibrium under different geochemical, temperature, and pressure conditions. Earlier developed analytical and numerical models, which take into account the microscopic heterogeneity of multimineral geosorbents and variations in the external chemical potential resulting from the rate-limited transformations of the mineral phase, will be applied (Part VII).

Chapter 21

Radon Site for Near-Surface Disposal of Solid RW

Radon Enterprise, as a regional repository for RW processing and disposal, is a member of the Northwestern Center of Nuclear Energy. The Center is located in Sosnoviy Bor Town (Fig. 21.1). The distance from the Radon site to the shoreline of the Gulf of Finland (Koporskaya Bay) is about 1 km.

The repository contributed to ensuring environmental safety. However, the engineering barriers designed to isolate RW sometimes fail to function to the full extent. Therefore, groundwater near the repository was polluted by radionuclides. In this context, of great interest is to assess the current water quality and to study the parameters that determine the intensity of migration process.

21.1 A General Description of the Groundwater Contamination Process

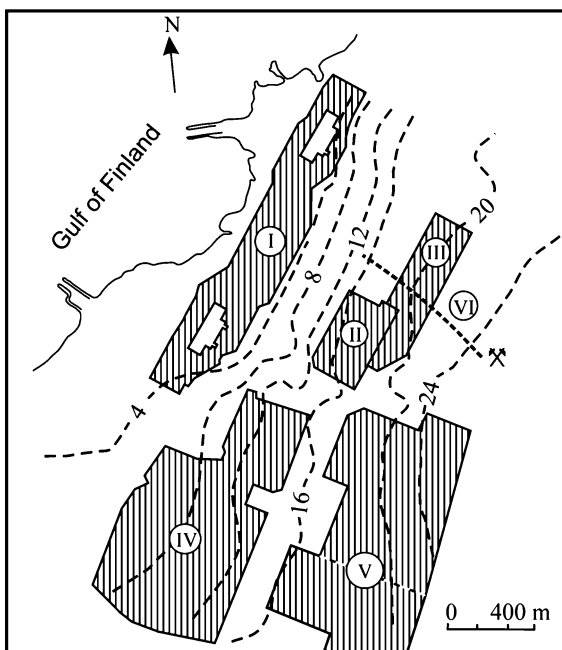
21.1.1 Hydrogeological Setting

Two aquifers are identified in the upper part of the section (Fig. 3.13), which is of particular interest in the context of the impact of RW repository on groundwater.

The first aquifer is confined to a *Quaternary* above-moraine sequence of sands with different genesis. The impervious floor of the aquifer lies between the absolute elevations of 1–24 m and slopes toward the Gulf of Finland. The aquifer thickness varies from 0 to 5 m. Its major portion is composed of dust and fine sands. The second aquifer is confined to sands and sandstones of the Lomonosov series of the *Cambrian*. The aquifer is underlain by a laminarite aquiclude. The aquifer thickness varies from 1–2 to 8 m. The horizons are separated by relatively impermeable clay deposits; however, this aquiclude is absent in some places and the aquifers show good hydraulic interaction here.

The piezometric surface of groundwater slopes toward the Gulf of Finland (Fig. 21.1), into which waters of the Cambrian and Quaternary aquifers discharge.

Fig. 21.1 A map showing the layout of construction sites of the Northwestern Center of Nuclear Energy combined with a map of piezometric surface of the Cambrian aquifer (*dashed lines, m*). (I) Leningrad NPP, (II) RW disposal facility of Leningrad NPP, (III) Radon RW disposal site, (IV) A.P. Alexandrov Technology Research Institute, (V) Leningrad NPP-2, (VI) EUR



21.1.2 The Causes and Extent of Groundwater Contamination

The first stage of Radon repository was put into operation in 1962. The total volume of RW placed for long-term storage was above 60,000 m³ (data as of 2008). The RW are currently housed in several buildings (Fig. 21.2).

Radioactive solutions originated because of seepage of atmospheric precipitation (rainfall and melted snow) water through solid radioactive wastes, which were placed in the buildings (of compartment/sectional style) with imperfectly designed waterproofing properties. During a period of around 10 years (1980–1990) a leachate percolated down to the Quaternary and Cambrian sand aquifers and migrated with the natural gradient flow towards the Gulf of Finland. The distribution of dissolved radionuclides in the aquifer shows temporal variations in the leachate leakage rates from different repository buildings. Unfortunately, radionuclide migration monitoring does not include an efficient leachate flow control system, and consequently, there is a degree of uncertainty in the solute transport analysis. The average rate of the radioactive solution release was estimated to be about 450 kBq day⁻¹ (Sr-90) and 24,000 kBq day⁻¹ (³H).

In 1990, the repository buildings were reconstructed, and the leakage rate was significantly reduced. At the same time, drainage operations were carried out to reduce groundwater level, thus facilitating the containment of subsoil water pollution and the rehabilitation of the area near the repository buildings.

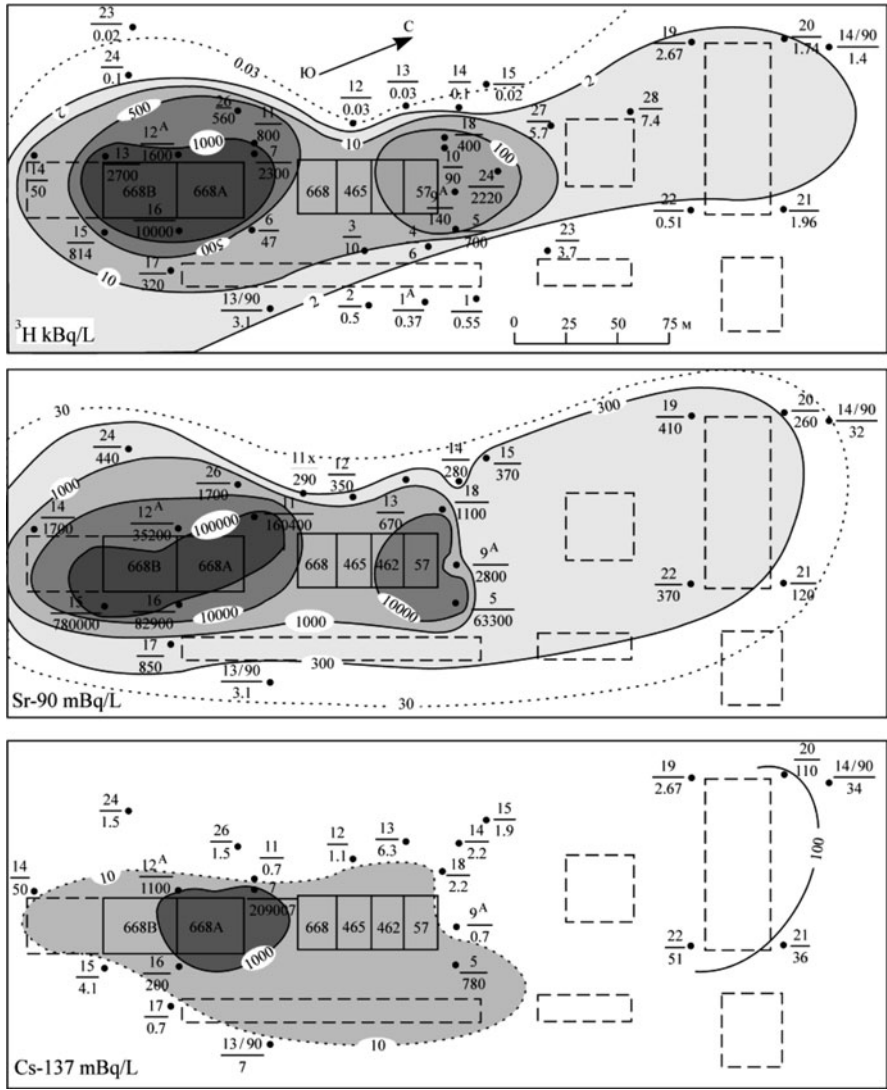


Fig. 21.2 Contours of radionuclide distributions illustrating groundwater contamination by different radionuclides at the Radon RW disposal site (1991, the maximum concentration levels). Black spots indicate observation wells (above line is the well number, below line is concentration). Rectangles show the contours of the buildings for RW disposal

As one may see (Table 21.1), the concentrations of the radiation doses generated by the major radionuclides in the leachate exceed the permissible values (maximum permissible concentrations, MPC), established by the State Safety Standards (UV/NRB-99). Moreover, the data given in Table 21.1 allow us to assess the efficiency of the repository facilities as protection barriers. Thus, the comparison of the

Table 21.1 Comparison of volumetric activities (BqL^{-1}) of leachates from the repository and groundwater taken from observation wells along the perimeter of the repository

Characteristic	^3H	Cs-137	Sr-90
Maximal values in the repositories (1998–1999)	$3.7 \cdot 10^7$	$7.4 \cdot 10^4$	$8.5 \cdot 10^3$
Mean values in the repositories (1998–1999)	$8.1 \cdot 10^6$	$1.1 \cdot 10^4$	$2.2 \cdot 10^3$
Mean values in the repositories (2009)	$4.9 \cdot 10^5$	$3.2 \cdot 10^2$	$6.7 \cdot 10^1$
Maximal values in wells (1990–1991)	$3.7 \cdot 10^7$	$6.7 \cdot 10^2$	$4.4 \cdot 10^3$
The same (1998–1999)	$1.9 \cdot 10^7$	$8.9 \cdot 10^1$	$9.3 \cdot 10^2$
The same (2006)	$1.6 \cdot 10^6$	$1.0 \cdot 10^1$	$3.0 \cdot 10^2$
The same (2009)	$9.4 \cdot 10^5$	$1.8 \cdot 10^1$	$2.8 \cdot 10^2$
Mean values in wells (2009)	$3.2 \cdot 10^{5a}$	–	$6.9 \cdot 10^{1b}$
Safety Standard Permissible Value (MPC)	7,700	11	5

^aAveraging over all wells within the site area

^bAveraging over the 7 wells where the volumetric activity exceeded the values, established by the Safety Standards (UV/NRB-99)

maximal activity levels of Sr-90 and Cs-137 in repository canyons and wells shows a considerable (up to one–two decimal orders of magnitude) difference between radionuclide concentrations in leachates and groundwater. The protection functions of repository facilities with respect to ^3H are less impressive.

The maximal effect of leakage from the repository on groundwater quality was recorded in 1990 (Fig. 21.2). Judging from the schematic map of pollution area distribution (Fig. 21.2), the most hazardous pollution sources are the buildings of 668, 668B, 668a, and 57. The leaks from these buildings contain different proportions of tritium and Sr-90, whose specific activities in some wells exceeded the background level by 5–7 orders of magnitude.

21.1.3 Dynamics of Groundwater Contamination

21.1.3.1 The Beginning Phase of the Process (the end of the 1980s through the 1990s)

As mentioned above, pollution fields were studied in detail in 1991. In this period, maximal radionuclide concentrations were recorded in the wells closest to repository buildings.

Some displacement of peak values of tritium and Sr-90 concentrations over time was observed in some wells, a possible cause being the sorption retention of the latter. Thus, higher pollution levels were recorded in well 7 during 1989–1991 (Fig. 21.3) with the strontium peak lagging behind the tritium peak by about 9 months. Later, a general drop in radioactivity was recorded. The length of one cycle is about 1 year, allowing the annual increase in radioactivity to be attributed to underflooding of basements.

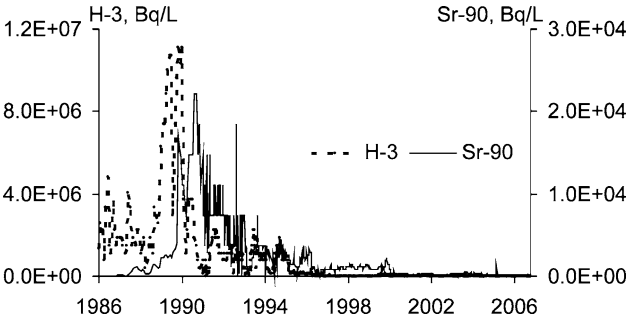


Fig. 21.3 Variance of tritium and Sr-90 concentrations as a function of time (observation well 7)

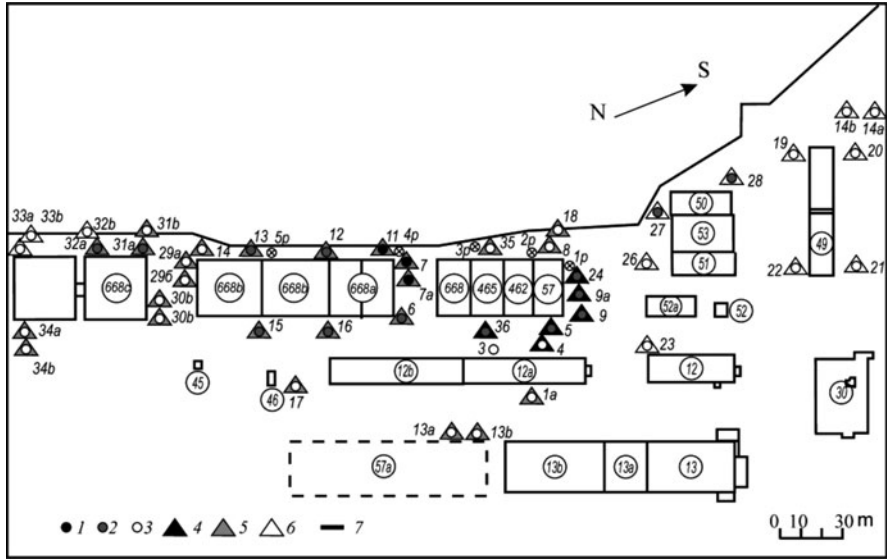


Fig. 21.4 Generalized monitoring data over 2006–2010. (1–3) The level of groundwater pollution by beta-activity (Sr-90): (1) heavy pollution (up to $n \times 100 \text{ Bq/L}$); (2) moderate (mostly up to $n \times 10 \text{ Bq/L}$); (3) no pollution (up to 5 Bq/L); (4–5) the same for tritium activity: (4) heavy (up to $n \times 10^5 - n \times 10^6 \text{ Bq/L}$), (5) moderate (mostly up to $n \times 10^4 \text{ Bq/L}$); (6) conventionally clean wells (mostly up to $7.7 \times 10^3 \text{ Bq/L}$); (7) the western boundary of the Radon site; figures are observation well numbers, figures in circles are building numbers

21.1.3.2 Groundwater Quality in the Current Term (2002 through 2010)

Analysis and generalization of data collected from observation well network over the period of 2002–2010 allowed such wells to be divided into three groups (Fig. 21.4):

- I. Wells detecting very high groundwater pollution level: radionuclide concentrations are tens to hundreds of times higher than the maximum permissible

concentrations (MPCs); graphs of $C(t)$ show that the natural attenuation (intrinsic remediation) is sufficiently slow, and the process exhibits a clearly pronounced stagnant character.

- II. Wells where concentrations are in excess of MPCs but the activity shows a distinct trend toward a decline; in some cases, radionuclide concentrations in water drop to admissible values; unexplained “spikes” of contamination in groundwater, many times greater than the background level, can also be recorded during this process.
- III. Wells characterizing unpolluted areas of the aquifer: radionuclide activity values here generally do not exceed the MPCs or even are close to background levels; no pollution was recorded in these wells throughout the observation period.

In terms of *beta-activity*, 30 observation wells are conventionally clean, 12 are moderately polluted, and 3 are heavily polluted.

The highest level of groundwater pollution, with maximal activity values of β -emitting radionuclides reaching tens and even hundreds of Bq/L, is recorded in the zone of “old” leaks near the building 668a (wells 7, 7a, 11). Close to the I group is also well 5, where a local peak in β -pollution was recorded in 2001–2002, after which the values dropped to a moderate pollution level. The high current pollution level of the wells of the I group is inherited from the previous period. Note that the current pollution level, though very high, is less than the pollution level recorded in the 1990s.

The II group includes several wells where distinct pollution peaks were recorded in the period in question, but a general trend toward groundwater rehabilitation (up to the recovery of background concentration) can be clearly seen. The wells of this group are located in zones adjacent to buildings 668, 668a, 668b, 465, 57, and 50.

The rest of the territory of Radon site does not feature groundwater pollution according to beta-activity values (wells belonging to the III group).

21.2 Variation in Sorption Coefficients and Controlling Factors

The intensity of migration process in the areas with existing and potential radioactive contamination of groundwater is largely determined by the natural hydrogeochemical conditions and rock (sediment) retention capacity (sorption–desorption processes). Experimental and model studies were used to examine the appropriate characteristics.

21.2.1 Distribution Coefficients (Linear Model)

It is well known that the coefficient of sorption distribution, K_d , is not perfect characteristics of migration of a reactive component (Sect. 20.1.1). Nevertheless, when

experiments with different samples are carried out under equivalent conditions, the obtained statistical distributions of K_d allow one to identify to which extent the chemical heterogeneity of an aquifer can affect the solute transport process. Nonlinear sorption effects will be considered later (Sects. 21.2.2 and 21.4).

The 100 samples of sand taken from the Cambrian weakly consolidated and unconsolidated sandstone near the Radon site differ in color. As a first approximation we can choose two color gradations: gray (both light and dark) and variegated (from yellow to reddish-brown) sandstone. The variegated sandstone occurs mostly in the top (about 1–2 m from the aquifer roof) part of the section, and its color seems to be due to the presence of larger amounts of metal oxides and hydroxides. This is a zone of primary interaction between infiltration and pore waters within which active oxidation–reduction processes take place (a kind of hydrochemical barrier). Thin seams of fine material also occur in gray sandstone underlying yellow and brown sediment varieties.

Sorption of Co-60, Cs-137, and Sr-90 was studied in the laboratory. The L:S ratio remained constant and equal to ten in all experiments ($V = 40$ mL, $m_s = 4$ g). The initial radionuclide concentrations were about 2,000 Bq/L. The error in estimating radionuclide activity did not exceed 10%. The number of calculated N-C-equilibrium points obtained in experiments with different radionuclides was 100, allowing reliable statistical analysis to be carried out.

To reveal statistical regularities (trends), distribution histograms of the coefficient K_d were constructed for both complete statistical samples (Table 21.2) and partial samples referring to one of the chosen colors. Note that all examined samples do not contradict to lognormal distribution law (Fig. 21.5). Moreover, the relationship between distribution coefficients and the concentration of oxidized metals in the samples was studied.

The coefficient K_d , which characterizes the adsorption of Co-60, showed sensitivity to the color scale (see Fig. 21.5, Table 21.3). The results of calculations given above suggest that the brightly colored sandstone varieties more actively absorb this radionuclide, and the darker the sediment, the larger K_d . Therefore, we can assume that there exists a relationship between the extent of radionuclide absorption by a sand and its content of metal oxides and hydroxides, which also determine the sand color (Sturgeon et al. 2006).

Table 21.2 Statistics of the distribution of $\ln K_d$ for Cambrian sands based on the analysis of generalized (without division by colors) of statistical samples

Radionuclide	Min	Max	μ_Y^a	$\sigma_Y^2{}^b$	CV_Y^c	N^d
Co-60	3.13	6.87	5.03	0.82	0.18	100
Cs-137	0.94	7.83	4.90	1.62	0.26	100
Sr-90	−1.72	1.92	0.73	0.37	0.83	100

^aMean ($Y = \ln K_d$)

^bVariance

^cCoefficient of variation, $CV_Y = \sigma_Y / \mu_Y$

^dNumber of samples

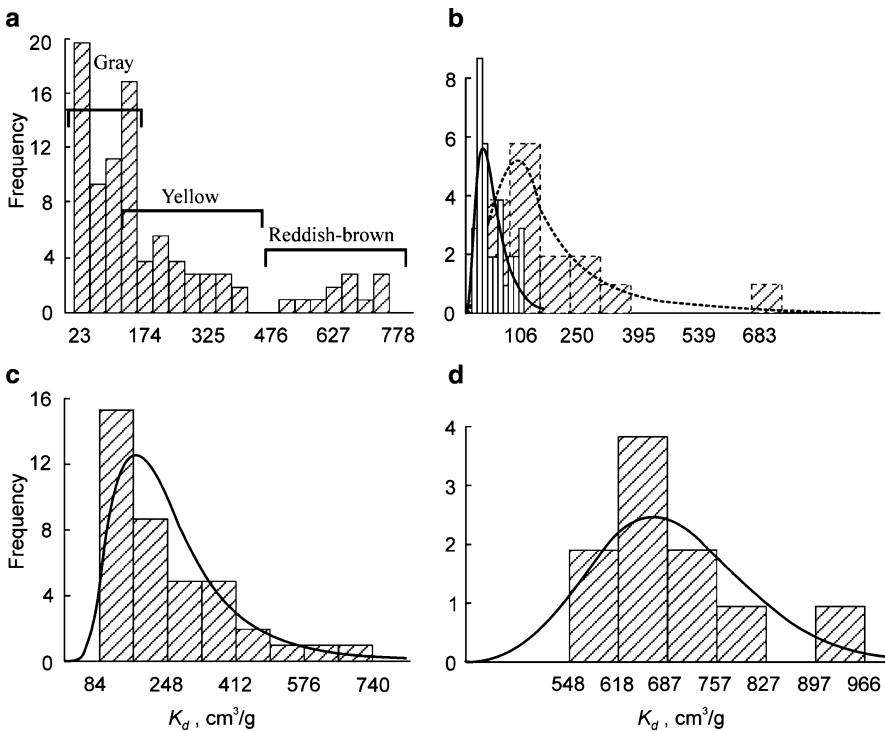


Fig. 21.5 Frequency distribution plots (histograms) of K_d for Co-60. **(a)** Generalized data, **(b)** gray sandstone (the *full line* refers to dry and the *dashed line*, to wet sandstone); **(c)** is yellow sandstone; **(d)** is reddish-brown sandstone. The points with $K_d > 1,000 \text{ cm}^3/\text{g}$ were excluded

Table 21.3 Statistics of the distribution of $\ln K_d$ for Cambrian sand by the results of analysis of statistical samples for Co-60

Color	Min	Max	μ_Y	σ_Y^2	CV_Y	N
Yellow	4.43	6.61	5.4	0.25	0.09	40
Reddish-brown	6.31	6.87	6.5	0.02	0.02	10
Gray	3.13	5.01	4.2	0.26	0.12	34
Dark gray ^a	3.51	6.63	5	0.61	0.16	16

^aSandstone with higher moisture content (near groundwater table)

Of interest in this context are the results of experiments with successive dissolution of mineral phase in hydrochloric, nitric, and hydrofluoric acid, making it possible to determine the total concentrations of some metals (Fe, Mn, Al, Na, K, Cs, Ca, Mg, Sr, Co, Cu, Pb, Cr, Ni, Zn, Ti) in some samples examined in sorption experiments. As can be seen from Fig. 21.6, the sorption distribution coefficient K_d shows a satisfactory linear correlation between sorption distribution coefficient K_d and the total iron and manganese content of rock. The points in the plot in Fig. 21.6

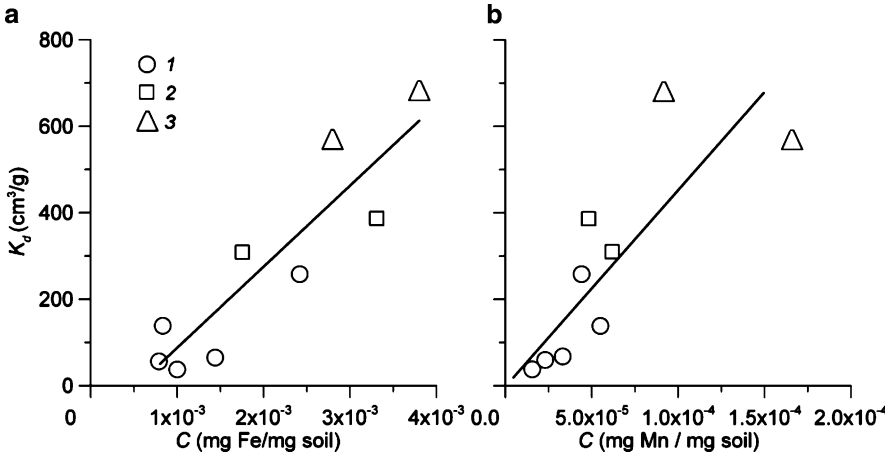


Fig. 21.6 Dependence of K_d on (a) iron and (b) manganese content of the sample. (1) Gray, (2) yellow, (3) reddish-brown sandstone

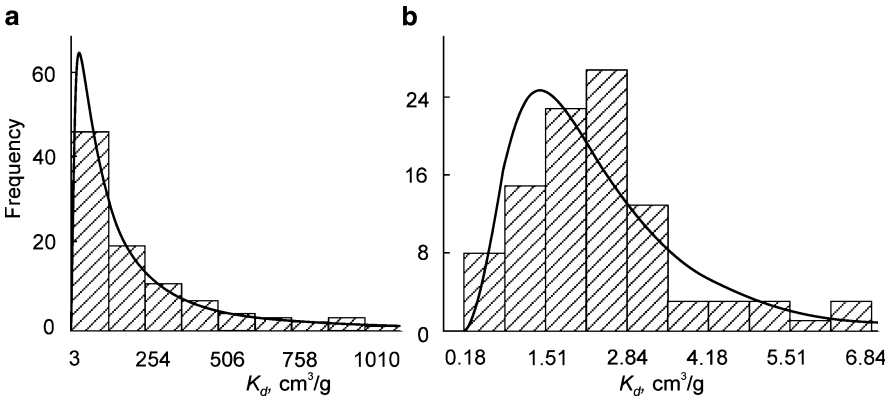


Fig. 21.7 Generalized histograms of K_d . (a) Cs-137, (b) Sr-90

that correspond to higher metal concentrations and the values of coefficient K_d refer to the darkest varieties of sandstones. The correlation between K_d of cobalt ions and the concentration of iron and manganese oxides and hydroxides in sediments is in good agreement with the studies of other authors (Anderson and Christensen 1988), who have come to the same conclusions.

In the case of radioactive isotopes of cesium and strontium, the statistical distribution was not found to have a significant correlation with sand colors and the concentration of oxidized metal forms. Other studies (Sabodina et al. 2008) also suggest a weak effect of oxide films on Cs-137 adsorption. Therefore, variations in K_d are described by generalized histograms (Fig. 21.7), whose characteristics are given in Table 21.2.

The comparison of the obtained results (Tables 21.2 and 21.3) shows that, by the degree of adsorption by studied aquifer material the radionuclides form the following series in descending order of mean values of K_d : Co-60, Cs-137, Sr-90. In this series, we can mention the higher values of the coefficient of variation, CV , of W_Y for the latter two terms of this series relative to that of the first term.

21.2.2 Nonlinear Freundlich Sorption of Co-60

In addition to the above analysis of variations in the sorption distribution coefficients, we give isothermal relationships obtained in experiments with Co-60 (Fig. 21.8). The nearly linear shape of the plots in bilogarithmic coordinates suggests the possibility to approximate the experimental data by the Freundlich equation (19.2). A correlation was found to exist between the linear coefficient K_F and the color series (Table 21.4): the variegated varieties of sandstones yield higher values of K_F . However, the exponential constant (the isotherms have about the same slope with respect to the abscissa, Fig. 21.8) varies only slightly, and no significant correlation was found to exist between n and K_F . Such behavior of the system can be explained, if we assume that different but equal in volume samples contain different numbers of “elementary” particles that have equal sorption parameters (K_F, n). These particles seem to be represented by iron hydroxides, which determine the color of sandstone. This fact shows the process to be controlled by a single type of chemical interaction. Otherwise, the plots would consist of a family of intersecting curves.

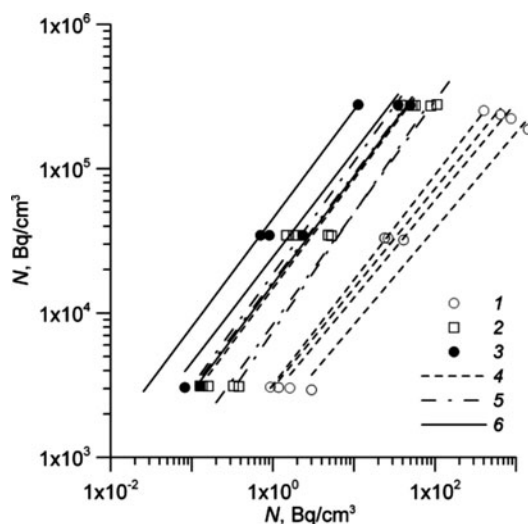


Fig. 21.8 Sorption of Co-60. (1–3) Experimental points: (1) is G, (2) is Y, (3) is RB; (4–6) are approximations of experimental points by the relationship (19.2): (4) G, (5) Y, (6) RB; colors: G is gray, Y is yellow, RB is reddish-brown

Table 21.4 Freundlich sorption constants

Sample code	K_F	n	Color ^a
A1	8,318	0.77	Y
A2	7,446	0.82	Y
A3	18,624	0.78	Y
A4	2,685	0.68	G
A5	3,173	0.73	G
A7	15,816	0.75	RB
A8	45,081	0.75	RB
B1	14,806	0.76	Y
B2	41,368	0.63	Y
B3	16,456	0.74	Y
B4	1,798	0.66	G
B5	3,028	0.69	G
B7	24,394	0.73	RB
B8	62,906	0.67	RB
Statistics (for normal distribution)			
Parameter	μ	σ^2	CV
K_F	$1.9 \cdot 10^4$	$3.2 \cdot 10^8$	0.94
ϕ	0.73	0.0025	0.07

^aG is grey, Y is yellow, RB is reddish-brown

21.3 Hysteresis in Sorption

Monitoring data on radionuclide temporal and spatial distributions indicate that natural attenuation process is currently taking place (Sect. 21.1.2). It is clear that the efficiency of the site natural attenuation is controlled by the ability of the rock matrix to release the earlier adsorbed radionuclides, and therefore the experimental study of desorption plays an important role in prediction of groundwater contamination. The other factor affecting the natural attenuation, namely the spatial variability of sorption coefficients, will be considered later.

21.3.1 Experiments with Reference Samples of Cambrian Sands

21.3.1.1 System Description and Experimental Setup

Several series of laboratory experiments with radioactive solutions containing strontium (Sr-90) and cesium (Cs-137) were carried out to study sorption-desorption processes.

Solution. The liquid phase in sorption studies was represented by model formation water with mixed cation and anion composition, mg/L (mg-equiv/L): Na^+ – 69 (3), Ca^{2+} – 20 (1), Mg^{2+} – 12 (1), Cl^- – 71 (2), HCO_3^- – 183 (3), Sr^{2+} – 0.1. Solution pH was 8.3. The desorption of radionuclides, simulating the replacement of waters with radioactive pollution by natural waters at the stage of natural attenuation of the site, was made by the same solution.

Soil. The natural adsorbent included three typical lithological varieties of sands sampled in an open pit near the Radon site. The sand samples differed in their color: 1c was yellow, 1n was white, and 2b was light-gray (the indices c, n, and b correspond to the sampled layers in the section, i.e., the middle, bottom, and top).

Studies of *particle size distribution* in the samples have shown the sample 1n to be relatively high in dust (up to 3.2%), silt (up to 3.3%), and clay (up to 2.5%) fractions. Conversely, the sample 2b is low in these fractions (0.3, 0.1, and 0.2%, respectively). Sediment sample 1c occupies an intermediate position.

The results of *X-ray structure analysis* allow us to make the following conclusions regarding variations in the mineralogy of the examined sediment samples (Table 21.5).

Sample 1n. This sample contains a mixed-layer phase of illite–smectite with about 80% of illite and 20% of smectite seams. With decreasing fraction size in this sample, the share of smectite component increases, but the total illite–smectite ratio remains almost unchanged. In the same direction, the concentrations of gypsum and lepidocrocite also increase, while that of quartz decreases. By major minerals, the sample can be classified as *kaolinite-illite* with admixtures of *quartz*, *gypsum*, and *lepidocrocite*.

Sample 1c. This sample also contains mixed-layer illite–smectite phase (with illite and smectite content of 80% and 20%, respectively), though in a lesser amount than in the previous sample. With decreasing fraction sizes, the share of smectite component increases; the illite-to-smectite ratio remains the same, but their total concentration in the sample drops by about 20%. Similarly to the sample 1n, the concentrations of gypsum and lepidocrocite increase and that of quartz decreases with decreasing fraction sizes. However, unlike the previous sample, lepidocrocite occurs in this sample in considerable amounts, seemingly determining its yellow color. By its major minerals, the samples were classified as *kaolinite-illite-lepidocrocite* with admixtures of *quartz* and *gypsum*.

Sample 2b. The predominant phases in this sample are gypsum and quartz. Clay minerals occur in lesser amounts, which are also much less than those in samples

Table 21.5 Concentrations of major minerals by fractions in the samples (weight %)

Minerals	Fraction diameter, mm								
	0.05–0.01			0.01–0.002			<0.002		
	1n	1c	2b	1n	1c	2b	1n	1c	2b
Illite	32	23	13	31	23	13	30	19	14
kaolinite	56	44	21	54	45	22	58	34	20
Quartz	12	6	20	10	4	13	2	<1	11
Gypsum	<1	2	42	5	5	35	8	6	41
Lepidocrocite	<1	25	–	<1	26	–	3	42	–
Halite	–	–	4	–	–	20	–	–	14

1n and 1c. The illite-to-smectite ratio remains unchanged (80% and 20%). Its main minerals classify the sample as *gypsum-kaolinite-illite-halite* with an admixture of *quartz*.

The examined sediments can be seen to contain minerals that considerably differ in their sorption properties; therefore, the microheterogeneity (caused by the existence of different types of sorption sites on the mineral phase) can be expected to affect the character of experimental data.

Tests' setup. Each series of sorption experiments used a sediment charge with a mass (m_s) of 2 g. The volume of experimental solution (V_1) was 20 mL. Thus, the liquid to solid ratio was the same in all experiments, L : S = 10. To identify the types of sorption isotherms, we used several initial concentrations, C_i , of radionuclides: 3,700, 370, and 37 Bq cm⁻³.

The decrease in radionuclide concentrations in solution ($\Delta C = C_i - C_0^s$, C_0^s is the equilibrium concentration) was used to evaluate the appropriate radionuclide concentration on the solid phase:

$$N \equiv N^s = \frac{(C_i - C_0^s) V_1}{m_s / \rho_b}, \quad (21.1a)$$

where, as can be seen, this concentration is converted to the concentration per unit sediment volume with dry bulk density, $\rho_b = 1.6 \text{ g cm}^{-3}$.

To calculate radionuclide concentration on the unconsolidated rock (in solid phase) during desorption, the following balance formula was used:

$$N \equiv N_{i+1}^d = N_i^d - C_{0i}^d \frac{V_2}{(m_s / \rho_b)}; \quad (21.1b)$$

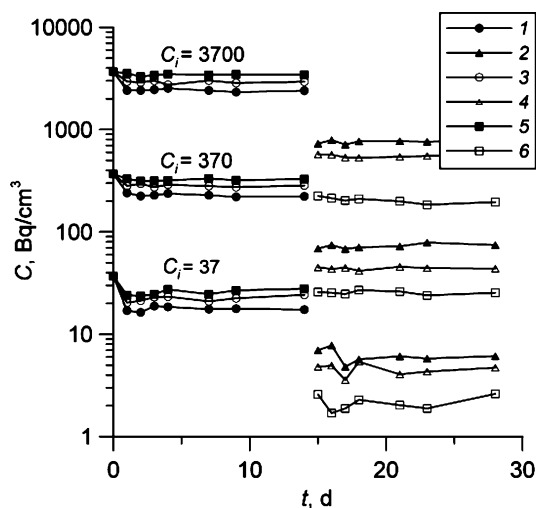
here N_i^d and N_{i+1}^d are the concentration on the solid phase at the i th and $(i+1)$ th desorption steps, C_{0i}^d is radionuclide concentration in solution after equilibrium has established at the end of the desorption step, V_2 is the volume of added "background" solution ($V_2 = V_1$ was assumed in all experiments).

The sorption experiment proper was preceded by a period of multistage saturation of Cambrian sand with model formation water until natural ionic equilibrium (Table 21.6). The treatment time of each sample with solution (L : S = 10 : 1) was

Table 21.6 Variations in solution cation composition during the preliminary treatment of sand samples

Cycle	pH			Cation concentrations, mg/L								
				Ca			Mg			Fe		
	1c	1n	2b	1c	1n	2b	1c	1n	2b	1c	1n	2b
I	8.43	8.46	8.51	15.2	15.7	15.9	9.4	9.9	10.3	0.93	0.80	0.85
II	8.26	8.51	8.51	14.5	14.1	13.6	10.0	10.5	10.3	0.87	0.90	0.83
III	8.48	8.42	8.45	13.8	13.7	13.1	12.3	12.3	12.2	0.82	0.87	0.97
IV	8.53	8.56	8.47	13.0	12.9	12.6	12.7	12.6	12.3	0.87	0.83	0.95
V	8.40	8.37	8.37	12.8	12.5	12.6	12.6	12.4	12.5	0.90	0.90	0.97

Fig. 21.9 Kinetic curves of sorption and desorption of Sr-90 at different initial concentrations of C_i . (1, 3, 5) Sorption on samples 1c, 1n, 2b; (2, 4, 6) desorption from samples 1c, 1n, 2b



3–4 days. The cation concentrations in the liquid phase after contact with sediment that are given here have been obtained by averaging data on six samples. These data show that five cycles of sediment treatment by solution lead to perfect stabilization of cation composition. This allows us to assume that the subsequent sorption-desorption experiments proceed under equilibrium thermodynamic conditions.

21.3.1.2 Qualitative Description of Experimental Results

It involved the analysis of the kinetic and equilibrium stages of experiments.

Process kinetics. Experimental data (Fig. 21.9) suggest a very fast kinetics of both sorption and desorption processes: almost complete stabilization of the concentration function, $C(t)$, is observed as early as the first day from the beginning of sorption (or desorption) experiment. Therefore, data on concentration C in the experimental solutions measured 14 days after the beginning of experiments characterize an equilibrium state of the system and can be used to construct isothermal relationships.

Sorption and desorption isotherms. The specific features of chemical equilibria at different stages of the process (sorption or desorption) is illustrated by Fig. 21.10.

The sorption branches of these plots in bilogarithmic coordinates are of linear character. This shape of plots is typical of isotherms described by a power Freundlich equation:

$$N = K_F C^n \quad (\ln N^s = \ln K_F + n \ln C), \quad (21.2)$$

where K_F and n are linear and exponential constants.

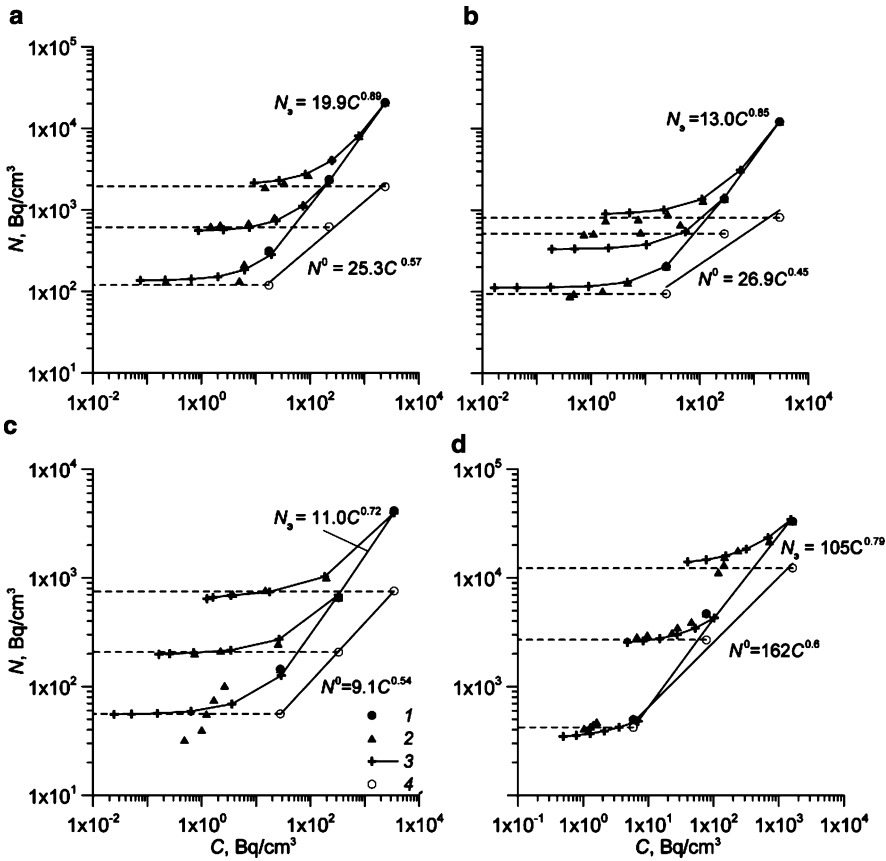


Fig. 21.10 Sorption-desorption experiments. (a, b, c) Results obtained for Sr-90 (on samples 1c, 1n, and 2b), (d) the same for Cs-137 (sample 2b). (1) Sorption, (2) desorption, (3) model interpretation, (4) concentration points of $N^0(C_0)$

A characteristic feature of all obtained desorption isotherms is their flattening in the domain of low concentrations: the isotherms generally tend to approach the “stationary” asymptotic $N(C) = N^0 = \text{const}$. This shows that the sand samples retains considerable amounts of radionuclides at their low concentrations in the solution in contact with the sediment. Moreover, no radionuclides were found to leave the sand at later desorption stages in some experiments ($C = 0$, $N = N^0$).

21.3.1.3 Interpretation of Experimental Results

Linearization of experimental relationships in coordinates $N^0 - C_0$ (19.8) allows one to evaluate the parameters $(1 - f)K_2$ and n_2 (Fig. 21.10, Table 21.7). Parameters fK_1 and n_1 (Table 21.7) were chosen by solving the system of Eqs. (19.15),

Table 21.7 Parameter estimates derived from the interpretation of experiments

Radionuclide	Sample	fK_1/K_1	$(1-f)K_2/K_2$	n_1	n_2	Effective isotherm ^a
Sr-90	1c	7.6/8	253/506	1.0	0.57	$20C^{0.89}$
	1n	3.8/4	269/538	1.0	0.45	$13C^{0.85}$
	2b	4.8/5	9.1/182	0.8	0.54	$11C^{0.75}$
Cs-37	2b	28.5/30	162/3,248	0.9	0.6	$105C^{0.79}$

^a $N_e = K_F C^{n_e}$ is a linearization of model points in the coordinate system $N-C$ with evaluated K_1 , K_2 , n_1 , and n_2 ; the dimension of K_i is $(\text{Bq}/\text{cm}^3)^{n_i-1}$

(19.13a), (19.13b), under conditions (19.16). With α_1^s , α_2^s , $\alpha_1^d \rightarrow \infty$ and $\alpha_2^d \rightarrow 0$, the model describes equilibrium reversible adsorption on first-type sites with the condition of irreversibility of adsorption on second-type sites being satisfied simultaneously. Suppose that 95% of the total mineral rock mass have low mass exchange (sorption) capacity (primarily, quartz), and 5% are active adsorbents of fine fractions (illite, kaolinite lepidocrocite); now $f = 0.95$. Simple calculations allow us to determine the absolute values of coefficients K_1 and K_2 (Table 21.7).

Analysis of the obtained data shows that the adsorption of Sr-90 (Fig. 21.10a, b, c) on fine, highly active fraction is described by strongly nonlinear isotherms $n_2 = 0.45 - 0.57 (\ll n_1)$. This fact accounts for the pronounced nonlinearity of the function $N^0 = f(C_0)$. Except for the sample 2b ($n_1 = 0.8$), sorption isotherms for first-type sites are linear ($n_1 = 1.0$). The model analysis of sensitivity has shown that all results are equivalent within the variation range of parameter $0 < \alpha_2^d \leq 0.01 \text{ day}^{-1}$, i.e., the issue of “absolute” irreversibility of the process (when α_2^d is strictly zero) is still open (we can speak only about irreversibility within the experimental time range).

The comparison of the obtained sorption parameters with data of mineralogical studies of samples shows that the adsorbability of Sr-90 mostly depends on the concentration of iron hydroxide (lepidocrocite) in the fine fraction of the samples. Thus, with the higher concentration of this mineral in sample 1c (25–42%), we have $K_F = 19.9$. The concentration of lepidocrocite in samples 1n and 2b is less than 1–3%, and the value of K_F drops to 11–13. At the same time, there is no direct correlation between the granulometric composition of samples and the estimates of linear constant K_F . Thus, at relatively high concentration of fine fraction in sample 1n (up to 8%), the sorption capacity of sediment is low ($K_F = 13$).

One can make such conclusions at a qualitative level by analyzing the experiments with Cs-137 solution (Fig. 21.10d). It is worth noting that the values of partial coefficients K_1 and K_2 are much higher than in the case of Sr-90; this fact is in agreement with the available data on the sorption capacity of rocks with respect to these radionuclides.

21.3.2 Model Estimates of the Formation of Concentration Fronts

We consider the results of calculation of concentration fronts for the conditions of averaged flows at the Radon site, by using a numerical solution of the system of equations (20.88), and the data of laboratory sorption experiments (see Sect. 21.3.1). The hydrodynamic parameters of the model are as follows: $q = 0.04 \text{ m day}^{-1}$ (the mean value of velocity at a gradient $I = 0.01 \text{ m/m}$ and the hydraulic conductivity $k = 4 \text{ m day}^{-1}$), $\phi = 0.3$, $\phi D_L = 10^{-5} \text{ m}^2 \text{ d}^{-1}$. The duration of the square-impulse concentration input $t_s = 5 \text{ yrs}$. We carried out three variants of calculations (Fig. 21.11) using sorption data for samples 1c, 1n, and 2b (Table 21.7).

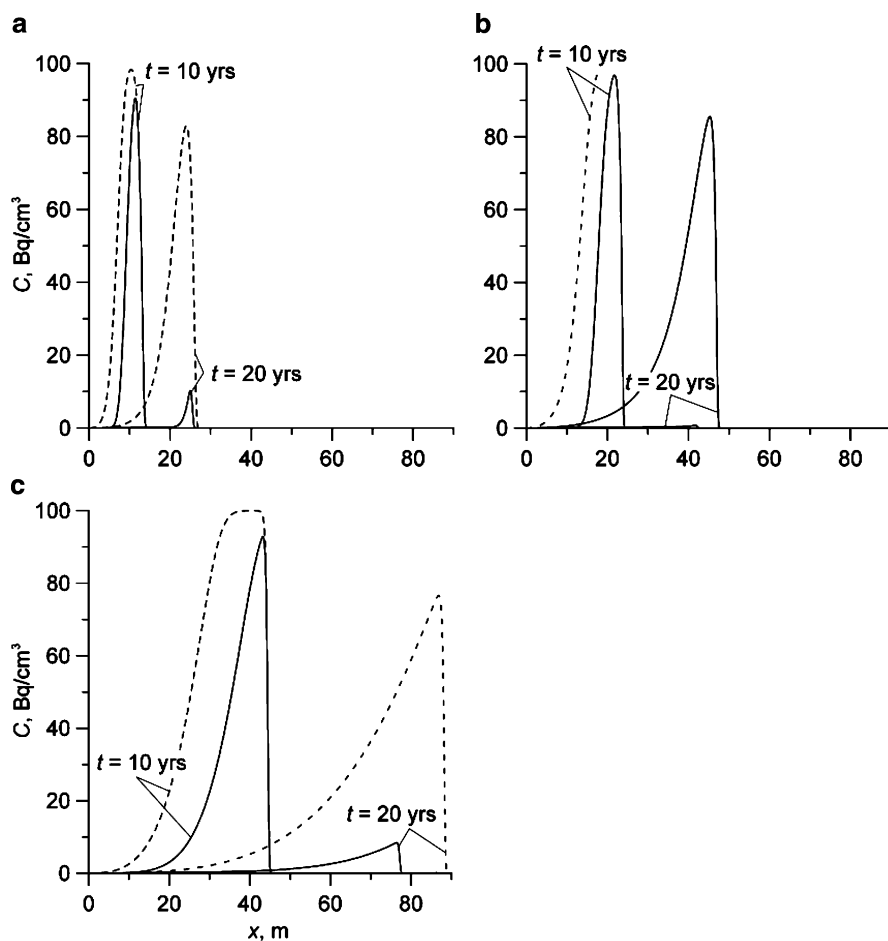


Fig. 21.11 Distribution of Sr-90 for 1D migration in typical varieties of Cambrian sands. Samples: (a) 1c, (b) 1n, (c) 2b. The *full lines* are for partially irreversible sorption, the *dashed lines* are for reversible sorption

As it was made with test examples (see Fig. 20.9), to illustrate the significance of the irreversibility of sorption process, the plots compare the calculation results with the case of reversible sorption ($\alpha_2^d \rightarrow \infty$). The results of calculations show that sorption irreversibility is among the main factors contributing to groundwater self-purification in this site. Moreover, the nonlinearity of the process leads to significantly asymmetric fronts – the leading sorption front is steeper than the trailing one.

At the same time, modeling shows that the difference between sorption parameters established in experiments cause difference in the propagation dynamics of concentration waves. This means that the spatial variability of sorption parameters may control the natural attenuation potential of the site.

21.4 Spatial Variability of Sorption Parameters

21.4.1 A Review of Published Materials

It is well known that the heterogeneity of water-bearing systems, generally understood as the spatial variability of hydraulic and physicochemical characteristics of rocks as a medium, is a key factor in the formation of groundwater pollution plumes (Bruesseau 1994). To study mass transport in such systems one has to combine the analysis of deterministic results of individual experiments with elements of stochastic description of the system as a whole. The development of models describing the combined effect of the two levels of heterogeneity on mass transport receives much attention in the hydrogeological literature (Kabala and Sposito 1991; Bellin et al. 1993; Dagan and Cvetkovic 1993; Gelhar 1993; Tompson 1993; Burr et al. 1994; Dentz et al. 2000a, b; Seeboonruang and Ginn 2006; Zavala-Sanchez et al. 2007). However, now it becomes clear that the efficiency of further theoretical studies is largely hampered by the lack of field data.

The overwhelming majority of publications are devoted to studying variations in rock (aquifer material) permeability (hydraulic conductivity, k). The spatial variations in the physicochemical characteristics of rocks have been studied on a very limited number of sites, the studies being mostly aimed at variations in the sorption distribution coefficient, K_d , as applied to individual types of pollutants (Robin et al. 1991; Tompson and Jackson 1996).

These publications mostly deal with porous (sedimentary, unconsolidated type) rocks, which often show an inverse correlation between K_d and k , which is due to the governing effect of clay fraction, whose higher concentration reduces sediment permeability, on the one hand, and increases its sorption capacity, on the other hand. However, it is important to note that in fractured rocks, zones with higher permeability generally feature higher sorption capacity. This is due to the fact that the rocks of such zones generally have more developed fracture systems and hence feature greater specific surface, resulting in an increase in the estimated coefficient of sorption distribution. Field data confirm this conclusion (Drozhko et al. 2007).

Statistical data on the characteristics responsible for nonlinear adsorption are given in very few publications (de Wit et al. 1995; Doring et al. 1998; Vereecken et al. 2000).

Thus, studies carried out at Krauthausen site (Germany) (Vereecken et al. 2000) show that the sorption of lithium and uranyl ions can be approximated by nonlinear Freundlich isotherms, which, in the case of lithium, demonstrate a very high non-linearity of the sorption process ($n = 0.37\text{--}0.69$). At the same time, a very weak correlation was found to exist between the sorption coefficients (K_F and n) and rock permeability. However, in the case of uranyl, the linear coefficient K_F was found to correlate well with the concentrations of fine and clay fractions in sediment and the cation exchange capacity. Variations in the exponential constant n did not feature any significant correlation with the characteristics mentioned above. Studies of lithium ion adsorption have shown that variations in the examined aquifer material properties have very weak effect on variations in the values of linear constant K_F . The exponential constant correlates with the concentrations of clay fraction and organic matter in the sediment. The behavior of lithium ions demonstrates a negative correlation between K_F and n .

Variations in the coefficient K_d and, obviously, other physicochemical factors are associated with the mineralogical heterogeneity of sediments and rocks (Viswanathan et al. 2003), the random or regular distribution of weathering products of primary minerals, forming secondary clay minerals or oxide (hydroxide) films of metals on the surfaces of mineral grains, though oxides and hydroxides can form independent phases in the form of inclusions. The presence of a clay component is reflected in the percent distribution of particle size and in the specific surface of a representative rock volume. The heterogeneous distribution of organic matter in the rock is an additional factor governing the variability of coefficient K_d (Macintyre et al. 1998). The neglect of variations in k against the background of wide spatial variations in K_d (or retardation factor, R) leads to simplified stochastic models. Nevertheless, their analysis is of great use for revealing important trends in the formation of groundwater contamination fields (Chrysikopoulos et al. 1992).

As mentioned above, parameter K_d can be either correlated or not correlated with the hydraulic conductivity, k . A model with negative correlation between K_d and k (Robin et al. 1991; Tompson 1993; Tompson and Jackson 1996) is most often used. The correlation between K_d and k can be less evident, and its existence may be revealed only in studying the correlation between a series of samples referring to individual zones in the aquifer. This conclusion has been derived from the analysis of field data collected at Borden site, Canada (Robin et al. 1991). The plots $K_d = f(k)$, as well as other functional relationships for K_d derived from experimental data commonly feature a considerable scatter of experimental points because of experimental errors and the difficulties to ensure the representativeness of individual samples in statistical ensembles.

Overall, the analysis of the published materials shows that correlations between sorption parameters (in particular, K_d), on the one hand, and the mineralogical, lithological, physicochemical, and other properties of rocks, on the other hand, are not always obvious and require much experimental efforts. Most often, the coefficients

of correlation are not high and experimental data suggest the potential effect of a combination of factors on variations in numerical values of K_d (Bruesseau 1994; Viswanathan et al. 2003).

In this section, in addition to assessing the heterogeneity of statistical samples, characterizing the variability of K_d , we try to find the spatial variations of the coefficients that govern nonlinear sorption interactions. Theoretical analysis of migration process in a heterogeneous medium with stochastic variations in hydraulic conductivity, k , and linear parameter of Freundlich isotherm, K_F ($n = \text{const}$), shows (Bosma et al. 1996) that the nonlinearity of the process appreciably shifts the estimates obtained for the case of linear sorption: (1) the dispersion of solutes (plume size) in the direction of the mean flow velocity is controlled to a greater extent by the nonlinearity coefficient n (with a decrease in n , the dispersion zone that forms in the case of an instantaneous input of a solute into groundwater flow increases as compared with the case of $n = 1$); (2) this effect is more significant than that of variations in k and K_F ; (3) the transverse dispersion is mostly governed by variations in the permeability field; (4) the size of the plume only slightly depends on the extent and character of the correlation between k and K_F ; (5) the mean velocity of plume displacement is governed by a combination of all parameters, including σ_Y^2 and σ_W^2 ($Y = \ln k$ and $W = \ln K_F$).

The random spatial variability of sorption parameters and nonlinear sorption are among the most important factors affecting groundwater remediation and natural attenuation of contaminated aquifers (de Wit et al. 1995). This conclusion is directly related to the Radon RW disposal site under consideration. Indeed, the experimental material discussed above showed that Cambrian sand is a natural geosorbent exhibiting both sorption nonlinearity and variability of sorption parameters depending on variations in mineral composition. To study this issue in more detailed manner, a special sampling program and laboratory sorption tests have been carried out.

The object of study was Cambrian sand (marine deposits). Sand samples were taken from shallow (up to 1.5 m in depth) boreholes during their hand drilling, as well as from a side of a construction pit. In all cases, the focus of studies was the correlation between sorption parameters and variations in porous medium properties and its material composition.

The samples were taken in different periods (2001 and 2006). Therefore, they can be assumed to represent two experimental series. These series differ in some methodological details in sorption experiments and a series of auxiliary experimental determination of the composition and structure of sand samples.

21.4.2 Spatial Variability of Nonlinear Sorption Parameters for Sr-90

21.4.2.1 Experimental Setup

The data for studying the spatial variability of Cambrian sand properties were collected from a regular grid of 37 shallow boreholes drilled for this purpose and spaced

at 5 m intervals. Two core samples each weighting about 300 g were taken from each borehole from depth of 0.5 and 1.0 m, making the total number of samples studied in the laboratory to be 74.

A procedure of laboratory sorption experiments, which was tested before under static conditions (Sect. 21.3.1), was used to obtain (a) Freundlich nonlinear sorption constants; (b) parameters responsible for the desorption of radionuclides. Radionuclide Sr-90 was used as a component being adsorbed. All samples were “conditioned” before sorption experiments. This procedure consisted in repeated washing of samples by a solution with the chemistry close to groundwater (Sect. 21.3.1), allowing us to carry out adsorption and desorption experiments under equivalent hydrochemical conditions.

Additionally, with the aim to assess the possible relationships and correlation between the physicochemical and physical properties of sediments, we studied the particle size distribution of sediments and their permeability (hydraulic conductivity k). For this purpose, the sand was sieved through a screen set with known sieve size, allowing each sand sample to be divided into fractions (in mm): greater than 10, 10–5, 5–2, 2–1, 1–0.5, 0.5–0.25, 0.25–0.1, 0.1–0.05, 0.05–0.01, 0.01–0.005, 0.005–0.002 and less than 0.002. The hydraulic conductivity was evaluated in a flow column.

21.4.2.2 Sorption Tests’ Interpretation

The main trends in the sorption of a radioactive strontium isotope are shown in Fig. 21.12. It can be seen that the majority of sorption isotherms follow the Freundlich relationship (19.2). In about 20% of cases, the experimental points, $N(C)$, can be seen to appreciably deviate from the theoretical isotherm. This can be attributed to experimental errors or the character of interaction between dissolved radionuclides and the rock matrix being more complex than that described by (19.2).

Linearization of experimental curves allowed us to evaluate the linear, K_F , and exponential, n , sorption constants for Sr-90 (Table 21.8). Analysis of these data suggests that the sorption process in general demonstrates a nonlinear correlation between N and C concentrations (the values of n were found to be much less than unit in most cases), while the constant K_F varies within a wide range of values. Thus, the porous medium can be regarded as significantly heterogeneous in terms of variability of its physicochemical characteristics.

Analysis of particle size distribution has shown that the samples are mostly represented by sand fraction (in mm) $0.05 < d < 0.5$. The total concentration of dust ($0.01 < d < 0.5$), silt ($0.05 < d < 0.01$), and clay ($d < 0.005$) particles varies within 2 to 5%. The mineral phase contains 93–97% of quartz grains (see also Sect. 21.3.1). The coefficient of heterogeneity C_u (d_{60}/d_{10} ratio) is less than 4 (with several exceptions). This means that sands are well sorted and homogeneous at the microlevel. Notwithstanding the low concentration of dust-silt-clay particles, they may determine the adsorption rate of radioactive strontium.

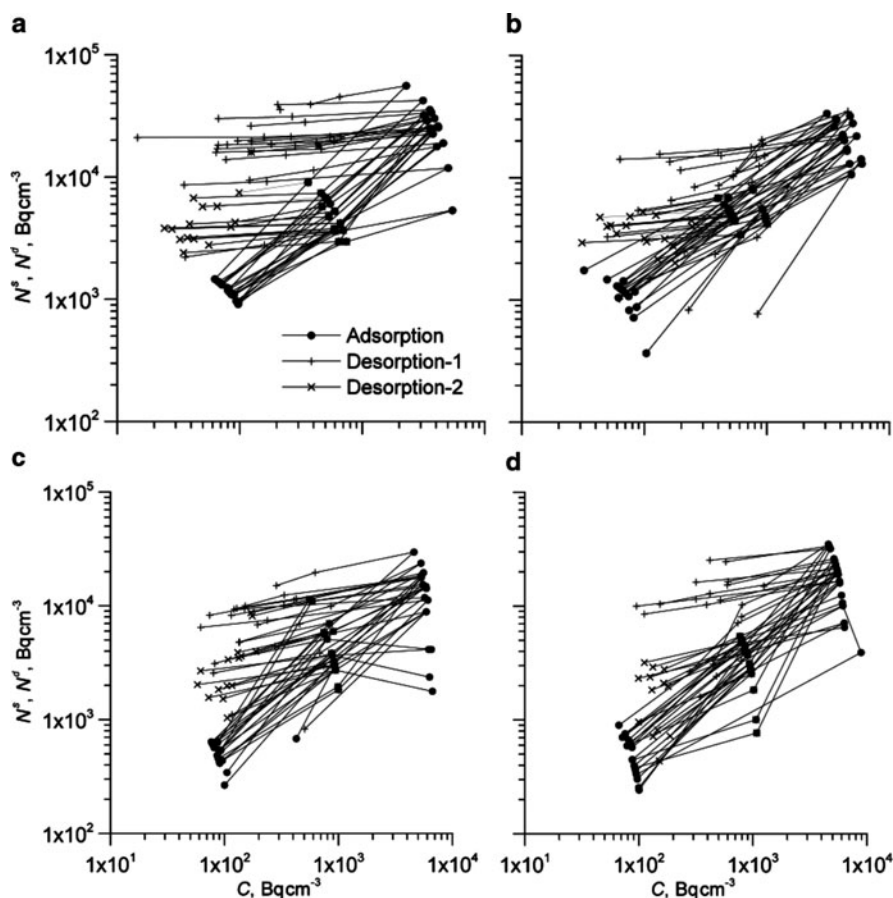


Fig. 21.12 Sorption-desorption isotherms for Sr-90. (a, b, c, d) Experimental series: (a) samples 1-1 to 9-2, (b) samples 10-1 to 18-2, (c) samples 19-1 to 27-2, (d) samples 28-1 to 37-2 (see Table 21.8)

Flow experiments showed the examined sand material has a relatively high permeability: k varies from 1.5 to 7.7 m day⁻¹ ($k_{\text{mean}} = 2.7$ m day⁻¹), which is in agreement with the data given before.

21.4.2.3 Histogram Analysis

To identify statistical variations and the distribution law of sorption constants (Table 21.9), we used standard statistical procedures. The analysis has shown the following:

- the linear Freundlich constant K_F has a longnormal distribution (Fig. 21.13a);
- the exponential Freundlich constant n (Fig. 21.13b) has a normal distribution.

Table 21.8 The results of interpretation of sorption experiments

B-I ^a	K_F	n	R^b	B-I	K_F	n	R	B-I	K_F	n	R
1-1	22.7	1.01	0.999	13-1	46.2	0.77	0.987	25-1	6.3	0.92	0.998
1-2	17.3	0.97	0.998	13-2	126	0.59	0.991	25-2 ^c	7.6	0.87	0.941
2-1	43.0	0.81	0.999	14-1 ^c	54.7	0.67	0.952	26-1 ^d	88.9	0.48	0.684
2-2	63.9	0.72	0.999	14-2	119	0.53	0.999	26-2 ^c	19.4	0.78	0.946
3-1	29.7	0.77	0.999	15-1	70.8	0.7	0.990	27-1	11.5	0.77	0.979
3-2	34.8	0.84	0.999	15-2	81	0.64	1.000	27-2 ^d	200	0.29	0.556
4-1	29.2	0.79	0.962	16-1	21.2	0.83	0.985	28-1	85.2	0.59	0.974
4-2	51.8	0.65	0.984	16-2	19.0	0.81	0.991	28-2	16.2	0.8	0.999
5-1	52.9	0.75	0.985	17-1	34.4	0.82	0.999	29-1 ^d	70.3	0.55	0.869
5-2	212	0.38	0.984	17-2 ^c	6.6	0.92	0.951	29-2	16.6	0.85	0.999
6-1	54.8	0.69	0.991	18-1	41.2	0.79	0.999	30-1 ^c	34.5	0.68	0.943
6-2	19.1	0.9	0.996	18-2	94.7	0.57	1.000	30-2	28.7	0.75	0.999
7-1	16.3	0.89	1.000	19-1 ^d	5.5	0.95	0.937	31-1	29.3	0.76	0.999
7-2	23.1	0.83	0.984	19-2	14.3	0.88	0.984	31-2	20.9	0.77	1.000
8-1	10.4	1.0	0.995	20-1 ^d	29	0.8	0.818	32-1 ^d	4.6	0.93	0.804
8-2	35.1	0.78	0.963	20-2 ^d	28.7	0.77	0.765	32-2	12	0.92	0.979
9-1	25.1	0.81	0.983	21-1	16.2	0.73	0.996	33-1	3.2	1.06	0.972
9-2 ^c	9.5	0.96	0.945	21-2 ^d	3.8	0.91	0.904	33-2	No data	No data	No data
10-1	43.9	0.82	0.999	22-1 ^d	103	0.45	0.844	34-1	3.5	1.02	0.983
10-2	30.7	0.83	0.998	22-2	9.5	0.88	0.999	34-2	2.7	1.02	0.999
11-1	43.2	0.74	0.999	23-1	3.9	0.94	0.983	35-1	1.7	1.1	0.994
11-2	73.8	0.65	0.997	23-2	10.9	0.94	0.999	35-2 ^d	4.9	0.91	0.920
12-1	206	0.6	0.995	24-1	18.4	0.78	0.999	36-1	5.2	0.92	0.996
12-2	145	0.59	0.998	24-2 ^c	222	0.31	0.959	36-2 ^d	17.5	0.66	0.885
								37-1 ^d	7.7	0.92	0.858
								37-2 ^d	3.6	0.93	0.788

^aBorehole number–interval number: interval 1 refers to the top ($z = 0.5\text{m}$) and interval 2 to the bottom ($z = 1.0\text{m}$)

^b R is correlation coefficient

^cIsotherms insignificantly deviate from the Freundlich curve ($0.94 < R < 0.96$)

^dThe deviation from Freundlich isotherm is considerable ($R < 0.94$)

The reliability of conclusions regarding the statistical distribution laws was confirmed by the comparison of experimental and theoretical cumulative distribution functions – the so-called P–P analysis (“probability–probability”) of plots (the results of this analysis are not given here).

Additionally, Table 21.9 gives the results of statistical analysis of the distribution of some additional characteristics: k , $C_u = d_{10}/d_{60}$, GSV, and SCPC. As can be seen, these parameters have a lognormal distribution.

Analysis of experimental data revealed a negative correlation between constants K_F and n (Fig. 21.14). A similar relationship was found to exist between coefficients K_F and n for lithium ions (Vereecken et al. 2000). This result differs from the conclusions obtained for Co-60 (see Sect. 21.2.2.), thus giving indirect evidence of different sorption mechanisms, whose manifestation in experiments with different

Table 21.9 Statistics for sorption and physical properties of the Cambrian sand aquifer

Parameter, y	$y_{\min}$	$y_{\max}$	y_{mean}	σ_y^2
$\ln K_F$	0.53	5.4	3.1	1.31
n	0.29	1.1	0.78	0.028
$\ln K_d^a$	-1.24	3.21	1.14	0.59
$\ln k^b$	-1.20	2.05	0.98	0.42
$\ln d_{60}/d_{10}^c$	0.41	2.30	0.86	0.076
$\ln SCPC^d$	-0.51	2.3	0.94	0.32
$\ln GSV^e$	-0.55	1.7	1.28	0.12

^aEffective distribution coefficient calculated for $C = 2,000 \text{ Bq/cm}^3$
^bHydraulic conductivity, md^{-1}
^cUniformity coefficient
^dSilty/clay particle content, %
^eGrain-size variance

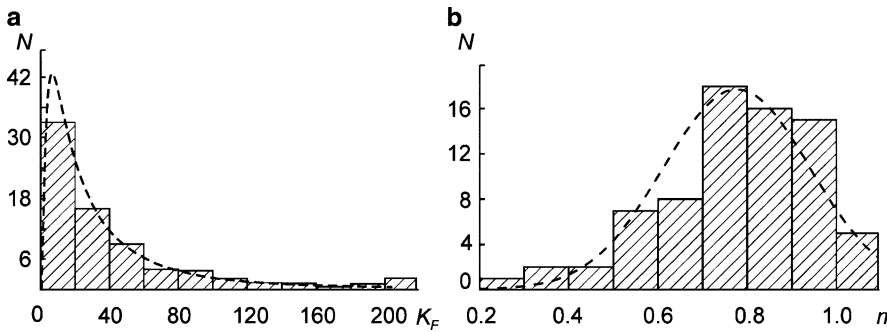


Fig. 21.13 Histograms of the Freundlich sorption constants (*bars* are experimental data; *solid lines* are theoretical distributions). (a) K_F , (b) n

radionuclides leads to such isothermal relationships. At the same time, the statistical analysis shows that the chemical constants are correlated neither with the studied grain-size distribution characteristics nor with the hydraulic conductivity.

21.4.2.4 Spatial Variability of the Freundlich Isotherm Coefficients

The relevant characteristics of spatial variability have been studied through variogram analysis. Two variogram subroutines from GSLIB (Deutsch et al. 1992) for irregularly spaced data in two and three dimensions were used. To handle two- and three-dimensional data, empirical semivariograms $Var(h)$ were calculated (Fig. 21.15) for four parameters ($Y_{(k)}$), $Y_{(1)} = n$, $Y_{(2)} = \ln K_F$, and $Y_{(3)} = \ln K_d$:

$$Var(h) = \frac{1}{2N(h)} \sum_1^{N(h)} [Y_{(k)i} - Y_{(k)j}]^2,$$

(21.3)

Fig. 21.14 The character of correlation between sorption constants. (1, 3) The depth: (1) $z = 0.5$, (3) $z = 1.0$ m; (2, 4) analytical approximations of the dependence $n = f(K_F)$: (2) $n = 1.15 - 0.11 \ln K_F$, (4) $n = 1.2 - 0.14 \ln K_F$

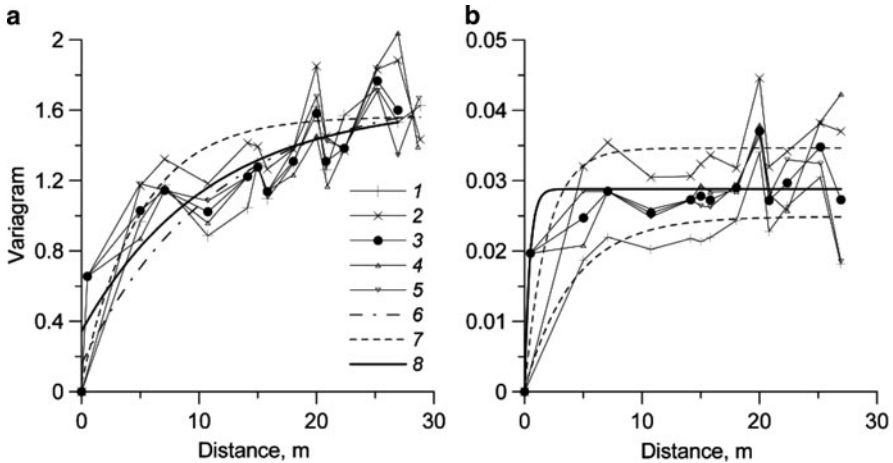
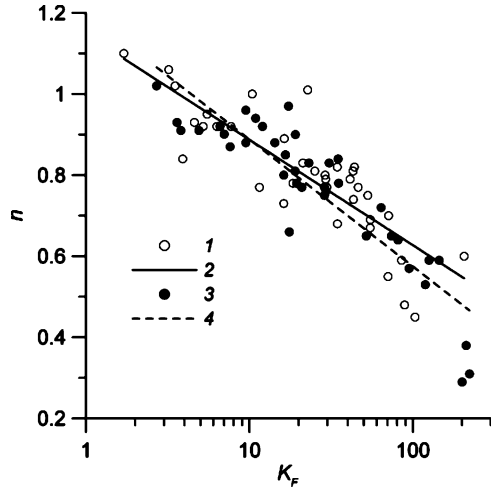


Fig. 21.15 Experimental semivariograms (*broken lines*) of sorption parameters and functions approximating them (*smooth curves*). (a) K_F , (b) n . (1) 2D, $z = 0.5$ m; (2) 2D, $z = 1.0$ m; (3) 3D (all points, tolerance 90°); (4) 3D (X , 45°); (5) 3D (Y , 45°); (6) 2D-var. ($z = 0.5$ m): (a) $0.16 + 1.54(1 - \exp(-h/12.0))$, (b) $3 \cdot 10^{-4} + 0.02(1 - \exp(-h/3.4))$; (7) 2D-var. ($z = 1.0$ m): (a) $0.045 + 1.5(1 - \exp(-h/5.0))$, (b) $2 \cdot 10^{-5} + 0.03(1 - \exp(-h/1.9))$; (8) – 3D-var.: (a) $0.34 + 1.3(1 - \exp(-h/10.8))$, (b) $-7 \cdot 10^{-7} + 0.03(1 - \exp(-h/0.43))$

where $N(\mathbf{h})$ is the number of pairs; $Y_{(k)i}$ is the value at the start (or tail) of the pair i ; $Y_{(k)j}$ is the corresponding end (or head) value; and $\mathbf{h}$ is the separation vector, which is specified with some direction and distance (lag) tolerance.

Two-dimensional analysis focused on the construction of variograms based on two sets of data obtained for each sampling interval ($z = 0.5$ m and $z = 1.0$ m). For three-dimensional variogram-analysis, the two intervals were considered to belong

to one data set. The semivariograms were calculated in all directions, including two perpendicular. Appropriate estimates showed that there is essentially no anisotropy in the $Y_{(1)}$, $Y_{(2)}$, and $Y_{(3)}$ fields. Mean semivariograms (in all directions) were therefore calculated and approximately fitted to theoretical curves $\gamma(h)$ of the standard exponential type:

$$\gamma(h) = c \left[1 - \exp \left(-\frac{h}{a} \right) \right]. \quad (21.4)$$

The fitted constants a and c are presented in the plot legends of Fig. 21.15. It appears that a certain number of pairs on the variograms was not sufficient to perfectly fit the exponential model.

The variograms for different sampling intervals were fitted to the exponential model with different ranges and sill values. The range of $\ln K_F$ is comparable with the size of the studied site. The range of n is about one-third of the size of the tested site. The variograms show a nugget effect.

Because of the wide scatter of points on variograms we cannot conclusively say that there exists any spatial correlation between parameters. It is likely that the data obtained at the chosen sampling scale do not contradict the hypothesis that the statistical parameter field is random and not correlated. The deviation of experimental points from theoretical curves may also be a result of the number of pairs of sampling points being too small. Analysis of the above data suggests that the variograms for different intervals can be approximated by theoretical curves with different sills and distances (ranges) at which the values of function $\gamma(h)$ become practically stable. The range for $\ln K_F$ is comparable with the size of the examined area (site). The range for n is one-third of site size. The character of variograms demonstrates a nugget effect determined by parameter σ_n^2 .

The shortcomings of the obtained information can have their effect on the accuracy of the probabilistic maps of sorption parameter distributions (these maps will be considered later); however, they cannot radically affect the conclusions at a qualitative level.

21.4.2.5 Geostatistical Interpolation of Sorption Constants

Two-dimensional contour maps of expected values of $Y_{(x)}$ (for each sampled interval of z) were constructed with the help of interpolation using kriging procedure. Since the distribution of K_F is lognormal, logarithms to the base e of the established values of this constant were used in this interpolation. To interpolate the data from sampling points by kriging procedure, we used empirical semivariograms approximated by analytical dependence (21.4); the coefficients of this equation are given in the capture to Fig. 21.15. The parameter σ_n^2 , characterizing the nugget effect, also took into account. The interpolation grid for two-dimensional modeling included 101×121 equilateral blocks ($\Delta x = \Delta y = 0.25$ m). Thus, probabilistic values of parameters $M_{\gamma_{(k)}}$ were obtained for intermediate points between sampling sites with known values of sorption coefficients. Such procedure is referred to as condi-

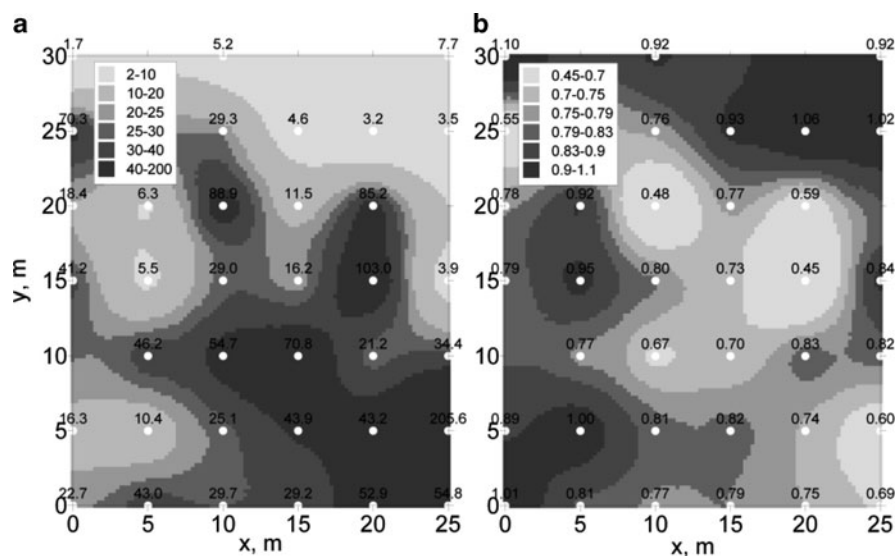


Fig. 21.16 Contours maps of sorption parameters (Sr-90, $z = 0.5$ m). (a) K_F , (b) n

tional simulation. The spatial distribution of $\ln K_F$ was transformed (Fig. 21.16) to obtain the distribution of constant K_F : $M_{K_F} = \exp(M_{\ln K_F})$. As it was expected, the inverse (negative) correlation between K_F and n has resulted in that the distribution maps of these constants look like a positive and negative photos of the same object

21.4.2.6 Variability of the Desorption Constants

The points of concentration measurement at the sorption and multistep desorption stages for all sets of experiments are shown in Fig. 21.12. The partial sorption-desorption constants have been estimated based on the dual-site model (Sect. 19.1.3.2). The fitting curves satisfactorily describe only about 40% of the experiments with Sr-90. The remaining 60% of the experiments could not be properly interpreted in the context of the model, probably due to experimental errors in the detection of low Sr-90 concentrations in solution and to the heterogeneity of the sand samples (two desorption branches belonging to one isotherm actually reflect the solution's chemical interaction with two sub-samples, which may differ at the microscopic level). Therefore, the available information is rather restricted in its use for comprehensive geostatistical analysis and generalization. Meanwhile it should be noted that (1) the variability of the calculated constants is significant, (2) in comparison to the relationship between apparent constants K_F and n , there is a similar correlation between the linear, K_i , and exponential, n_i , partial Freundlich constants.

Overall, the material given in Sect. 21.4 suggests that sands are highly heterogeneous in terms of variations in the parameters that control radionuclide sorption

and desorption. At the same time, variations in the examined physical parameters that characterize the dispersivity of the porous material and its permeability are relatively small, and the stratum is relatively homogeneous in this aspect. Because the sampling points are concentrated within a relatively small area, we failed to obtain an unambiguous estimate of the values of spatial correlation scale. Therefore, additional studies, which are of general scientific interest, should be carried out in this direction.

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Chapter 22

Study of Physical, Mechanical, Flow, and Solute Transfer Properties of Clay Formations with Respect to the Design of Underground Storage Facilities for RW Disposal

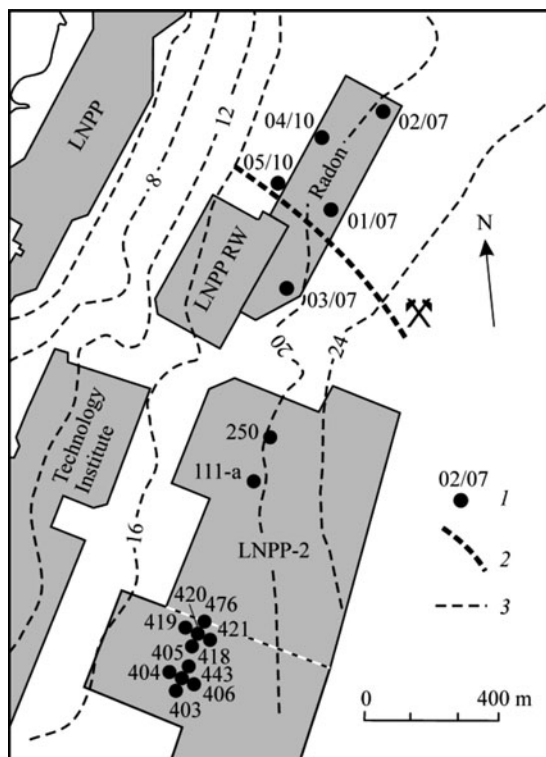
22.1 Introduction Remarks

Clay formations are widespread in the Northwestern part of Russian Federation. In St. Petersburg region southeast of the Gulf of Finland and Ladoga Lake, they occur close to the surface (Fig. 22.1). The sediments are represented by two formations, which formed in Vendian and Cambrian geological periods ($\sim 650\text{--}500$ Ma). The degree of the clayey sediment consolidation is rather high and therefore they can be also referred to the mudstone lithological type of rock (Arnould 2006). In the northwestern Russian Federation, Vendian and Cambrian clays have local names, Kothlin (associated with a geological suite) and Blue (associated with the characteristic color), respectively.

The clays having low permeability and high sorption capacity are considered to be a suitable host environment for toxic or radioactive waste (RW) repositories. To quantify the barrier and geotechnical properties of these geological units and to assess the potential impact of engineered RW repository on the environment, field observations and laboratory experiments as well as modeling studies have been carried out in 2006–2011.

Several key sites were selected for detailed field description and testing of collected clay samples. The sites are scattered in the St. Petersburg region south and east of the Gulf of Finland. The Radon site (the existing repository for solid RW disposal, see Chap. 21) is selected as the primary candidate for the designing of underground RW repository (URWR). Three sites with borehole-clusters (Leningrad NPP-2, Radon, Metro-2), and a site (Metro-1) related to mined subway tubes were sampled in detail. Several samples were collected from shallow excavations (Nikolsky and Krasny Bor open pits). In total, more than 300 core-bore samples and rock-monoliths for laboratory examination and testing were taken from the key sites. The collected samples were used to study a set of physical and mechanical (geotechnical) characteristics of rocks, as well as flow and mass-transport parameters. More than 20 parameters characterizing physical and geotechnical (strength and deformation) properties were assessed. Discontinuity networks in pits, shallow excavations, and subway tubes were observed and documented.

Fig. 22.1 Layout of engineering-geological boreholes at Radon and LNPP-2 sites. (1) Engineering-geological borehole and its number; (2) the route of underground mine (Engineered URW); (3) isoline of hydraulic head (Cambrian aquifer)



Data on the physicochemical, radionuclide-retention, diffusion, and geomechanical (geotechnical) properties of Kothlin (**Vkt**) and Blue (**CBlue**) mudstones obtained elsewhere as well as data on the relevant properties of clay formations in the Western Europe were collected and analyzed. In particular, a preliminary comparative analysis of the Vkt and CBlue clay properties against the results of the study of Rupelian Boom clay at Mol (**BC**) (Belgium), Callovo-Oxford argillaceous rocks (siltstone-silty clay) at Bure (**COx**) (France) and Aalenian Opalinus clay (**OPA**) at Mont Terry (Switzerland) has been performed (Arnould 2006; Bock et al. 2006; Huysmans and Dassargues 2006; Rumynin et al. 2009). These formations were selected as potential host formations for the disposal of HLW (high level and long lived radioactive waste).

Unlike the BC, Cox, and OPA formations in Western Europe, where clays are overlain by thick (hundreds of meters) sedimentary rock strata, the clays in the northwestern region of the Russian Federation lay near the surface at depth not more than a few tens of meters. As compared with BC, Cox, and OPA clays, the Vkt and CBlue clays are more loose and subject to exogenous processes. Therefore, these clays show high spatial variations in physical properties and the sensitivity to the distribution of external load.

Currently, the most likely option for the construction of underground RW repository in northwestern Russian Federation is the area coinciding with the existing Radon surface RW repository (Fig. 22.1). This area is close to the construction site of the Leningrad NPP (LNPP-2), which has been a subject of detailed geological and engineering-geological studies. Therefore, the analysis that follows is largely based on the data of testing rock samples taken from the following boreholes:

1. 01/07, 02/07, 03/07, 04/10, and 05/10 at the Radon site;
2. 111 a and 250 (basements of nuclear reactors 1 and 2) and 418, 419-a, 420, 421, 476, 403, 404, 405, 406, 443 (basements of nuclear reactors 3 and 4) at the LNPP-2 construction site.

The collected and generalized data enable the assessment of spatial variations in various parameters of clay formations. These parameters can be categorized into two groups:

1. those determining the geotechnical conditions of the underground repository construction and operation (strength and deformation), and
2. those controlling the safety of the repository from the viewpoint of radiation impact on the environment (flow and solute transport properties).

The main results of the study of engineering and solute transport properties of clays will be discussed below.

22.2 The Structure, Chemical and Mineral Composition, and the Physical Properties of the Clays

Micro-scale structure. The samples taken from the key sites demonstrate a micro-layered structure: silt layers from a few mm to 2 cm in thickness alternate with argillite layers, so one may expect some exhibition of *anisotropy* in the physical properties of the studied formations due to their sedimentary origin. The clay formation anisotropy is also a first important characteristic of the Boom, Callovo-Oxfordian, and Aalenian Opalinus clays.

Discontinuities in the clay formations. Field observations of geological outcrops, shallow (near-surface) excavations, underground mines and boreholes have shown that

1. the upper part of Vkt and CBlue clay formations, which outcrops near the surface, was found to be disintegrated by a fracture network of different genesis; the joints generated by a release of natural stress (decompression) and the effect of weathering are predominant;
2. the density of joints decreases when the clay is overlain by other geological layers;
3. only few fractures were identified by examining rock samples from boreholes; some fractures are sealed with secondary minerals; no significant shifts of lithological microlayers along fractures were found;

Table 22.1 The statistics of grain size distribution

<i>d</i> , mm		1–0.5	0.5–0.25	0.25–0.10	0.10–0.05	0.05–0.01	0.01–0.005	<0.005
Radon (V ₂ kt)								
Content %	Min	–	–	–	2.7	12.7	10.6	15.9
	Max	6.8	11.0	8.5	17.9	56.0	21.5	58.7
	Avr	1.2	1.9	2.5	8.3	29.9	15.7	40.5
LNPP-2 (V ₂ kt)								
Content %	Min	0	0	0.1	1.8	14.3	8.4	17.6
	Max	1.2	1.9	8.5	49.3	47.9	26.9	63.9
	Avr	0.1	1.2	1.6	12	23.1	16.5	45.5

- three sets of natural joints were revealed in mines related to the St. Petersburg subway tubes under construction: two of them are nearly vertical and can be associated with movements of the Archean and Proterozoic crystalline base of the territory; the third set, including horizontal joints, is connected with the clayey deposit formation. The walls of the natural joints are smooth and dry. The joints are closed, and no secondary minerals covering the walls were observed. They differ from artificial, *decompression* joints, which have rough walls; a typical distance between joints is around 20–30 cm.

Overall, the performed studies confirm the conclusions of M. Arnould (2006), who analyzed data on the fracturing of clay formations Boom Clay, Opalinus Clay and Callovo-Oxfordian Silty Clay. Thus, the comparison of data obtained by studying fracturing in near-surface open-pit mines, on the one hand, and the results of drilling and examining deep mine workings (immediately after their driving), on the other hand, shows fractures to exist only in the near-surface zones of sections and their formation to be caused only by weathering processes and the release of stress on the examined rock massifs. Only single fractures, if any, were recorded at large depths; this fact is in agreement with the results of drilling key wells at the Radon site. Not denying the existence of a sparse fracture network at large depths, M. Arnould (2006) stresses that the external compressive stresses in clays are quite sufficient to cause complete healing of fractures, thus ensuring the high water resistance of clay strata at the macroscopic level.

Grain size distribution. Most Vkt and CBlue clays contain >40–45% of clay particles (<0.005 mm). This is close to the content of fraction from 0.005–0.05 mm size-interval (Table 22.1; the number of experiments with different clays varies between 20 and 40).

Chemical composition and mineralogical constituents. The Vkt and CBlue clays consist of oxides of silicon (>50%), aluminum (>15%), iron (>5), sodium (up to 2%), and magnesium (up to 6%). The pelitic fraction (<0.01 mm) of the clay shows the presence of principal clay minerals, quartz, and orthoclase. Illite dominates among the clay minerals (Table 22.2, Vkt clay).

Table 22.2 Mineralogy of the pelitic fraction of Vkt clay (borehole 01/07, Radon site), %

Interval, m	Illite	Kl ^a	Chl ^b	Interval, m	Illite	Kl	Chl
20.1	70	25	5	57.0	74	20	6
22.8	71	22	7	68.7	75	19	6
27.1	76	19	5	76.6	74	20	6
35.2	67	27	6	86.1	76	19	5
37.9	73	22	5	87.1	76	18	6
43.2	76	16	8	98.2	62	32	6
47.3	71	24	5	114.6	52	45	3
49.4	76	18	6	127.7	35	61	4
55.9	70	24	6				

^aKaolinite

^bChlorite

Table 22.3 CEC variations (Radon site)

Interval, m	CEC ^a	W ^b	Interval, m	CEC	W
Borehole 01/07					
20.50–20.65	6.0	12.4	77.00–77.15	6.8	10.5
36.80–36.95	5.3	13.9	88.30–88.45	8.3	10.4
48.45–48.60	9.0	13.9	97.90–98.05	5.3	9.6
58.20–58.35	7.5	12.2	111.45–111.60	3.0	9.8
65.95–66.10	5.3	12.1	117.95–118.05	0.8	13.3
			133.25–133.40	4.5	10.0
Borehole 02/07			Borehole 03/07		
16.20–16.35	7.8	13.5	15.95–16.10	6.0	13.8
23.35–23.50	6.0	13.0	23.25–23.40	5.3	11.8
36.85–37.00	10.7	12.6	44.95–45.10	10.5	12.2
45.80–45.95	10.3	13.3	48.50–48.65	9.0	13.7
59.35–59.50	8.3	12.0	58.45–58.60	5.3	11.0
68.60–68.80	5.3	11.6	65.75–65.90	6.0	10.7

^aCation exchange capacity, mg-equiv/100 g.

^bMoisture content, %.

Cation exchange capacity (CEC). The Vkt clay shows rather low (for a clayey type of sediments) values of CEC: the average value is 6.6 mg-equiv/100 g (Table 22.3). CEC of the CBlue clay varies between 10.2 and 13.4 mg-equiv/100 g.

The chemical and isotopic composition of pore water. The examination of the core material (using aqueous extract technique) from borehole 01/07 (Radon site) shows that profiles of the principal-cation concentrations in pore water versus depth are somewhat variable (Fig. 22.2). This tendency is in agreement with data on isotopic pore water composition (Fig. 22.2).

Summary of physical properties. The following clay physical properties were tested: field moisture content, W ; bulk density, ρ_b ; bulk density of dry sediment, ρ_{bd} ; density of particles, ρ_s ; porosity, ϕ ; moisture at the limits of yielding flow

Fig. 22.2 Cation and ^{18}O concentrations versus depth (borehole 01/07, Radon site)

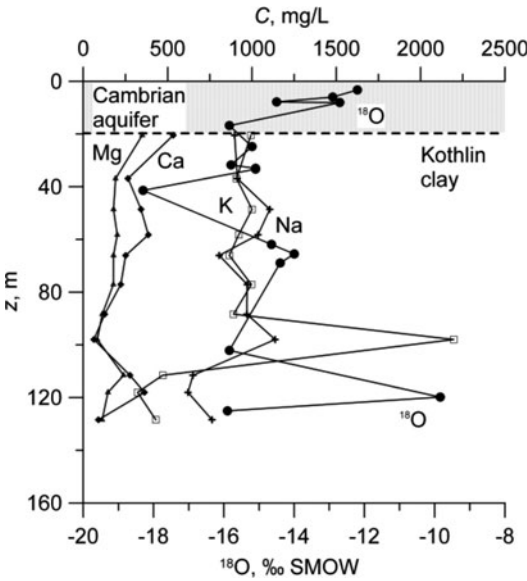


Table 22.4 Physical properties of the Vkt clay (Radon site)

Characteristics	Min	Max	Mean	CV ^a
W , %	7.1	22.5	13.62	0.15
ρ_b , g/cm ³	2.09	2.42	2.24	0.02
ρ_{bd} , g/cm ³	1.71	2.26	1.97	—
ρ_s , g/cm ³	2.65	2.81	2.73	0.012
ϕ	0.19	0.31	0.25	—
W_L , %	20.7	40	30.65	0.14
W_P , %	14.4	27.0	20.55	0.14
PI , %	4.1	17.6	11.87	—
S_r	—	—	0.95	—

^aCoefficient of variation

(liquid limit), W_L ; moisture at the limit of plasticity (plastic limit), W_P ; plasticity index, PI ; saturation, S_r . Thorough laboratory examinations of 77 samples from five boreholes (1/07, 2/07, 3/07, 4/10 and 5/10) at the Radon site have established statistically representative variation ranges of physical parameters of the Vendian clay as shown in Table 22.4.

22.3 Rock Mechanical and Hydraulic Properties

The mechanical properties of the CBlue and Vkt clay formations have been characterized by triaxial (under drained and undrained loading conditions) and uniaxial compression tests. The results obtained made it possible to determine a complete set of mechanical parameters, e.g., modulus of general deformation, E_0 ; modulus

Table 22.5 Geomechanical characteristics of the clay formations

Parameters	Unit	CBlue, OPs ^a	Vkt, Radon	Vkt, Metro-1
Cohesion, C	MPa	0.15–0.3	0.2–0.35	2.5–3
Friction angle, φ	Degree	10–20	20–35	10 (?)
Uniaxial strength, σ_c	MPa	0.3–0.4	0.9	2.5–7.5
Modulus of deformation, E_d	MPa	50–60	40–120	970–1300
Poisson's ratio, ν		0.35–0.4	0.2–0.3	0.2–0.3

^aOpen pit sites (Nikolsky and Krasny Bor open pits)

of deformation, E_d ; shearing resistance, C , and the angle of shearing resistance, φ ; uniaxial compression strength, σ_c ; Poisson's ratio, ν (Table 22.5). When analyzing the laboratory data, one has to take into account that when the core assigned for testing is lifted up to the surface, the decompression tends to exaggerate the microfractures openings, while they are more close under natural stress conditions. This may result in erroneous geotechnical parameters.

The hydraulic properties of the Vkt clay formation have been characterized by core flow tests. They were performed under elevated-pressure conditions using modified triaxial equipment. Two samples 50 mm in diameter were cut out from each block sample intended for tests in such a manner that flow was directed along the bedding in one sample and across it in the other sample. Overall, five experimental series were carried out.

The obtained values of hydraulic conductivity varied from $4.6 \cdot 10^{-11}$ to $2.2 \cdot 10^{-10}$ m/s along the bedding and from $5.8 \cdot 10^{-12}$ to $1.6 \cdot 10^{-11}$ m/s across it. Thus, the clay massif shows an appreciable anisotropy in permeability.

22.4 Variations in Physical and Mechanical Properties over Depth

Examination of data from lab experiments with core samples allows us to establish a clear tendency in the spatial variations in physical and mechanical properties of the studied clay formations. Thus, a comparative analysis of samples from different borehole intervals has arrived at significant coefficients of correlation for the parameters that characterize the degree of the clay water saturation, compaction, and consistency (field moisture content, bulk density, and porosity) with depth (the elevation of the core-bore sample in the profile) (Fig. 22.3).

As follows from plots in Figs. 22.3a,b, the rocks in the upper zone (I) of the section (down to the depth of 40–50 m) are relatively loose because of the effect of physical weathering and the small weight load from the overlying mantle rock. The lower zone (II) is represented by denser and drier rocks: the rocks at depths below 40–50 m were protected against the direct impact of external factors, such as glaciers and marine transgressions; their properties have formed under the effect of higher natural load caused by the weight of the overlying rocks.

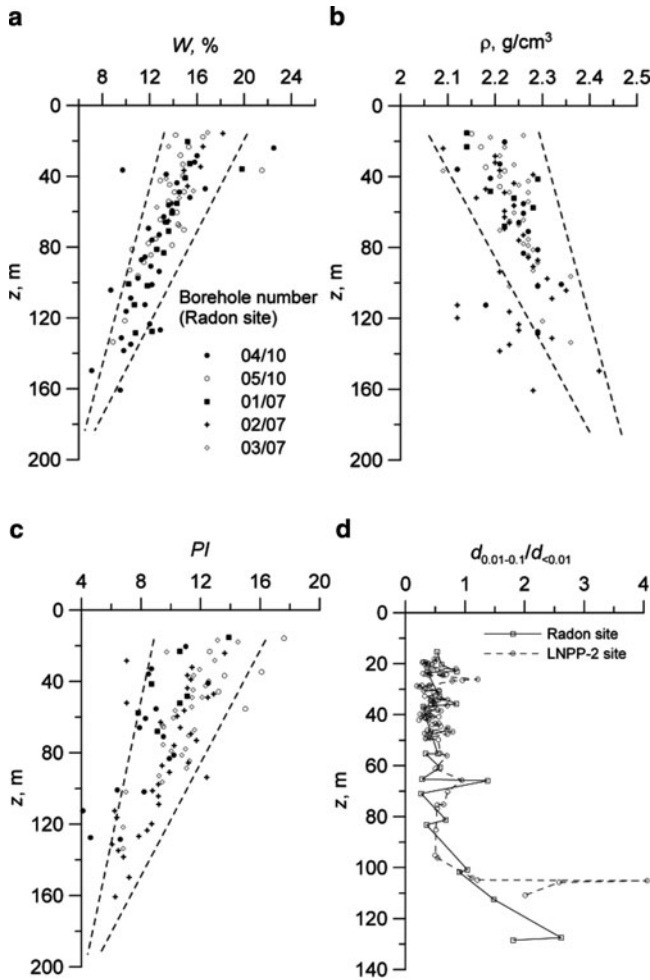


Fig. 22.3 (a) Moisture content, (b) rock density, (c) plasticity index, and (d) $d_{0.01-0.1}/d_{<0.01}$ ratio vs. depth (Vkt clay)

The decrease in the plasticity index with depth (Fig. 22.3c) most likely demonstrates that the silt-size particle content has a tendency to increase with depth. The latter conclusion is confirmed by the increase in the ratio $d_{0.01-0.1}/d_{<0.01}$ of clay fraction particles to silt fraction particles (Fig. 22.3d).

The rock deformation and strength parameters also demonstrate a dependence on the depth (Figs. 22.4–22.6). Thus, the deformation modulus of the rock mass increases with increase in the depth of sampling, suggesting a decrease in rock compressibility at large depths (zone II) as compared with near-surface zone (I) of the studied profile (Fig. 22.4).

The differences between the strength characteristics of the upper (I) and lower (II) parts (zones) of the cross-section are illustrated by plots obtained from triaxial

Fig. 22.4 Variations in the modulus of deformation of soil with depth. (1) Radon site, (2) LNPP-2 site, $z = 0$ is the top of the Vkt clay

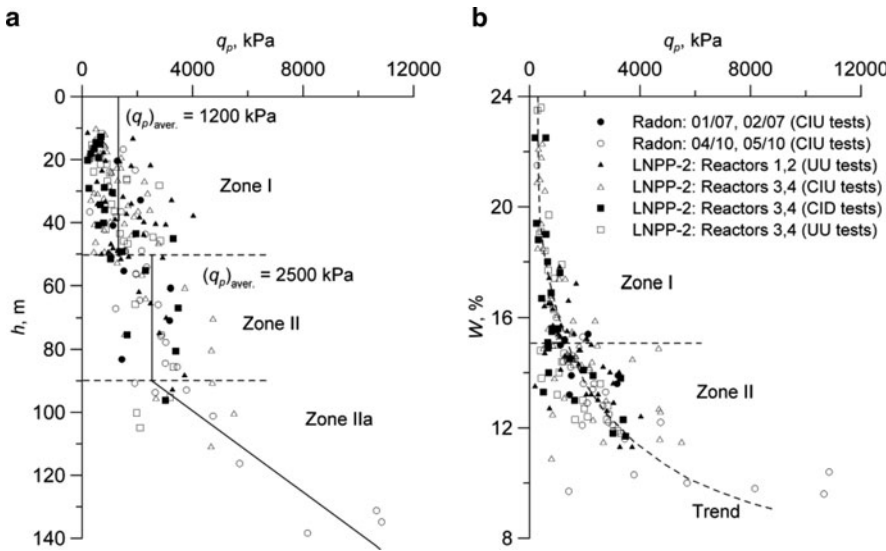
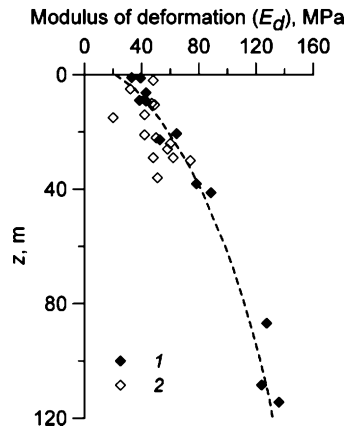


Fig. 22.5 (a) Variation of peak deviatoric stress from *UU*, *CID*, and *CIU* triaxial tests, q_p , with depth, h ; (b) correlation of q_p with moisture content, W

experiments with samples taken from different borehole intervals (Figs. 22.5 and 22.6). The plots in Fig. 22.5a reflect the difference, $q_p = \sigma_1^p - \sigma_3^p$ (peak deviatoric stress), between the axial (vertical) breaking stress, σ_1^p , and volumetric (compression) stress, σ_3^p , vs. depth, h , and moisture content, W . The observed tendencies correspond to the case of clay increasing progressively in shear strength with depth. Also analyzing plot in Fig. 22.6b, one may suggest that physical parameter W essentially controls the consolidation degree of clay and hence the shear strength (it is well known that overconsolidated clays have higher shear strength than unconsolidated clays).

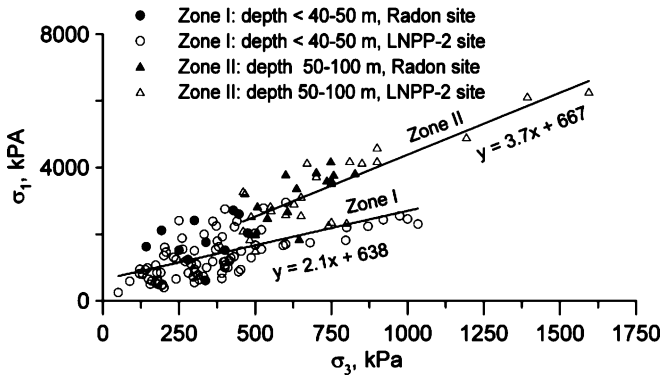


Fig. 22.6 Plot of triaxial strength test results for samples from different depth zones of Vkt clay formation together with fitted lines. Generalized data from UU, CID, and CIU triaxial tests. Data for *Zone IIa* are not presented

Table 22.6 Generalized data of triaxial tests of Vkt clay samples taken from Radon and LNPP-2 sites

Test type ^{d–g}	Zone I			Zone II		
	<i>C</i> ^a	φ ^b	<i>N</i> ^c	<i>C</i> ^a	φ ^b	<i>N</i> ^c
CIU ^d	279.4	18.1	48	265.5	32.1	26
UU ^e	184.5	23.2	30	354.6	27.6	16
CIU + UU ^f	231.9	20.7	78	310	29.8	42
CIU + UU + CID ^g	199.4	21	96	256.7	34.5	48

^aCohesion, kPa

^bFriction angle, grad

^cNumber of tests

^{d–g}Tests: ^disotropically consolidated undrained; ^eunconsolidated undrained; ^faveraged values (isotropically consolidated undrained + unconsolidated undrained); ^gaveraged values; ^g(isotropically consolidated undrained + unconsolidated undrained + isotropically consolidated drained)

The points on the strength plot (Fig. 22.6) show the dependence of the vertical breaking stress σ_1^p on the volumetric stresses σ_3^p : $\sigma_1^p = f(\sigma_3^p)$. The analysis of such representation of triaxial test data also reveals a pronounced trend toward an increase in rock strength with depth: the samples that were taken in the upper zone with depths down to 40–50 m from the surface (approximately, the *upper 30-m zone I* of Vkt clays) group around the first global trend line, corresponding to the strength properties, represented in Table 22.6. Most pairs of experimental values of σ_1^p/σ_3^p for samples from the *lower zone* (II) of the clay strata (depth interval from 50–55 m to 90–100 m) group near another global trend line, corresponding to higher rock strength characteristics (Table 22.6).

22.5 A Comparative Analysis of the Clay Formations

As mentioned above, underground nuclear waste disposal in clay geological formations is under intensive investigation in the Western Europe. The clayey rocks that are being investigated range from a rather plastic rock type (Boom Clay) to claystone (French and Swiss cases). The comparative Table 22.7 summarizes the main characteristics of these formations. The other Table 22.8 characterizes the basic mechanical properties of Vkt clay.

Analyzing the above two tables, one may conclude that the mechanical and hydraulic rock properties of different clay formations differ depending on (i) the age of the deposit; plastic clay types are younger, and have a higher porosity and water content; (ii) the elevation of the formation top that determines the pressure of overlying geological deposits and the natural stress conditions; thus, the strength of Vkt clay at the Radon site is noticeably lower than COx and OPA clays, however tests of clay samples from underground mines (Metro-1 site, 50–60 m bellow surface) show that the strength and deformation properties of Vkt clay are quite comparable with those of COx and OPA clays. The following consequence follows from the above comparative analysis: COx (cemented) > OPA $\approx$ Vkt-2 $\gg$ BC (plastic). All formations are characterized as formations with very low hydraulic conductivity: Vkt $\sim$ BC (–10 to –11) > OPA (–13) > COx (–14).

Table 22.7 Basic rock mechanical properties of the different clay formations for RW disposal in Western Europe (Verstricht et al. 2003; Wileveau and Bernier 2008)

	Boom clay (B)	Meuse/haute Marne (F)	Opalinus clay (CH)
Index	BC	COx	OPA
Geology	Rupelian (middle Oligocene)	Mid. Callovian– lower Oxfordian	Aalenian (Dogger)
Age	30 My	145 My	180 My
Thickness (m)	100	135	80–120
Burial depth (top) (m)	180	300–1,000	500–1,000
Clay minerals	60%	40–45%	40–80%
Bulk density (t/m^3)	1.9–2.1	2.3–2.6	2.5–2.6
Total porosity (%)	36–40	12–16	12–18
Hydr. conductivity (m/s) ^b	$2 \cdot 10^{-12}/4 \cdot 10^{-12}$	$<10^{-12}$	$8 \cdot 10^{-14}/2 \cdot 10^{-13}$
Uniaxial strength (MPa)	2.0–2.2	22–28	4–8
Young's modulus (MPa)	200–400	2,300–11,000	2,000–3,000
Poisson's ratio (–)	0.13	0.3	0.24–0.33 ^a
Cohesion (MPa)	0.3	7	1–3
Friction angle (°)	18	25	24
Plasticity index (%)	32–51	–	–

^aFrom Soe et al. (2009)

^bValues separated by/: values perpendicular/values parallel to bedding planes

Table 22.8 Basic rock mechanical properties of the Vendian clay for RW disposal at key sites

	Radon and LNPP-2 sites	Metro-1 site
Index	Vkt-1	Vkt-2
Age	530–650 My	530–650 My
Thickness (m)	100	120
Burial depth (top) (m)	5–20	20–40
Clay minerals	40–45%	40–45%
Bulk density (t/m^3)	2.0–2.3	2.3–2.5
Total porosity (%)	20–24	20–21
Water saturation (%)	12–18	9–12
Hydr. conductivity (m/s)	$1.4 \cdot 10^{-11} / 1.3 \cdot 10^{-10}$	–
Uniaxial strength (MPa)	0.4–1.6	2.5–7.5
Young's modulus ^a (MPa)	100–250	1,900–2,600
Poisson's ratio (–)	0.2–0.3	0.2–0.3
Cohesion (MPa)	0.2–0.45	2.5–3
Friction angle ($^\circ$)	20–35	10 (?)
Plasticity index (%)	7–14	8–10

^aThis parameter is assumed to be conventionally equal to doubled value of modulus of deformation ($E \approx 2E_d$, according to the results of two tests with Vkt clay sample from Metro-1 site).

22.6 Sorption–Desorption Experiments (Vkt Clay)

Retention of radionuclides (Sr-90, Cs-137, Co-60, Pu-239,240) due to sorption onto clay material was studied using samples from boreholes located at the Radon site (Fig. 22.1). We analyzed vertical variations in the values of sorption–desorption-related coefficients determined on Vkt clay samples collected throughout most of the clay formation section. Experiments were carried out with a synthesized solution with chemistry identical to that of the overlying Cambrian aquifer (mg/L): $\text{Na}^+ - 69$, $\text{Ca}^{2+} - 20$, $\text{Mg}^{2+} - 12$, $\text{Cl}^- - 71$, $\text{HCO}_3^- - 183$, $\text{Sr}^{2+} - 0.1$.

22.6.1 Sorption

Before the batch sorption experiments, clay samples were conditioned with a synthesized solution. The weight of each clay sample was $m_s = 1$ mg, the volume of radioactive solution was 40 mL (V_1), thus, $L : S = 40$. The sample was exposed for 7 days with periodic mixing. After this period, the volumetric activity of radionuclides in solution was determined by gamma-spectrometric analysis. Next, the clay sample, containing adsorbed radionuclides, was covered with fresh (radionuclide free) synthesized solution with a volume of 25 mL (V_2). The solid and liquid phases were in contact for 7 days also with periodic mixing. Three steps of desorption from clays were thus implemented to characterize all depth intervals. Besides, three samples from borehole 1 were used in 7-step desorption cycle.

As one may see in Fig. 22.7 and Table 22.9, the equilibrium distribution coefficient, K_d , varies in a wide range of values, depending on the nature of radionuclides.

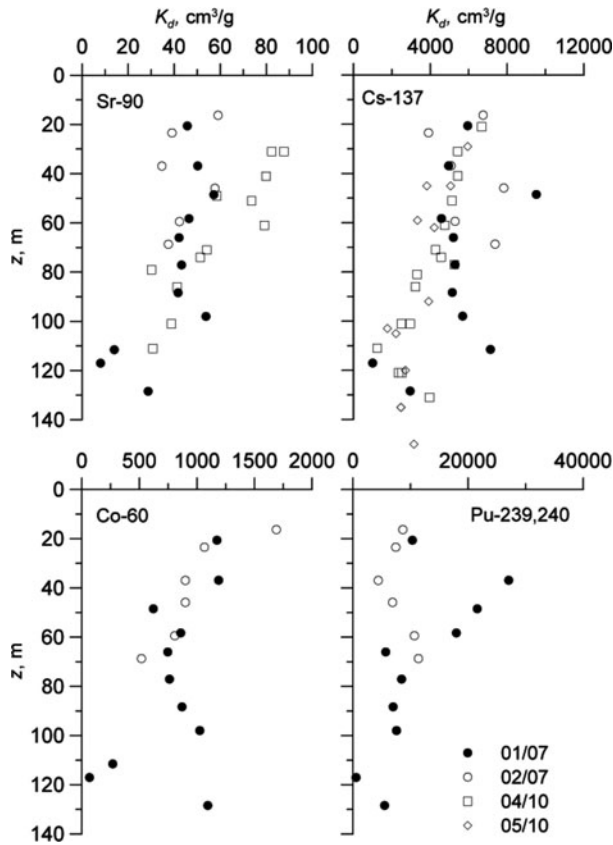


Fig. 22.7 Variation of sorption distribution coefficient with depth (integrated samples). 01/07, 02/07, 04/10, 05/10 are borehole numbers

Table 22.9 K_d range (cm^3/g) for different radionuclides

Radionuclide	Sr-90 ^a	Cs-137 ^c	Co-60 ^a	Pu-239,240 ^b
Depth up to 100 m				
Min–Max	34–59	3,313–9,520	518–1,830	5,676–36,492
Average	47	5,411	1,041	14,569
Dispersion, σ^2	7.9	1,365	344	9,035
Number of tests, N	14	26	20	14
Depth bellow 100 m				
Min–Max	8–29	993–7,131	66–1,094	541–42,226
Average	17	2,888	476	14075
Dispersion, σ^2	–	1,629	–	–
Number of tests, N	3	11	3	3

^aBoreholes 01/07, 02/07

^bBoreholes 01/07 and 03/07

^cBoreholes 01/07, 02/07, 04/10, 05/10

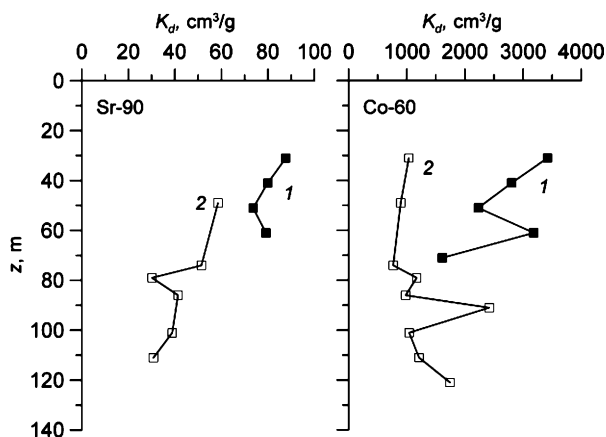


Fig. 22.8 Variation of sorption distribution coefficient with depth (borehole 04/10). 1 corresponds to integrated samples, 2 corresponds to samples taken from micro-layers represented predominantly by sand/silt fraction

The least sorbable is Sr-90, while Pu-239,240 is the most sorbable. Co-60 and Cs-137 occupy an intermediate position.

Experiments with Vkt clay (Radon site) showed weak negative correlation between K_d and depth (Fig. 22.7). The scatter of K_d values within sampling intervals is due to the lithological variations in the consolidated sediments, i.e., the alternation of layers with different content of sand/silt fraction that illustrates by Fig. 22.8.

22.6.2 Desorption

Analysis of the process is based on isothermal relationships ($N-C$), evaluated in the process of multistep desorption of radionuclides that have been adsorbed on the sediment at the first (adsorption) stage of experiments. Desorption experiments with plutonium isotopes, which gave a wide scatter of parameters, are not considered below. The initial (adsorption) point on $N-C$ plot was calculated from the decrease in radionuclide concentration in solution (21.1a). The bulk density of the clay was assumed to be 2.2 g/cm^3 . The balance equation (21.1b) was used to calculate radionuclide concentration in solid phase during desorption.

The experimental curves can be quite adequately described by two types of functions: for Sr-90, this is the linear isotherm ((19.1), Fig. 22.9a,b), and for Cs-137 and Co-60 this is the nonlinear Freundlich isotherm ((19.1), Fig. 22.9c, d). Analysis of the values of sorption coefficients showed that (1) the distribution coefficients $K_d \equiv K_d^d$ for Sr-90, which have been calculated from slope ratios of the straight lines (Fig. 22.7a,b) approximating the desorption points, are close to the values $K_d \equiv K_d^s$, obtained in sorption experiments (Table 22.10); (2) the desorption curves for Cs-137

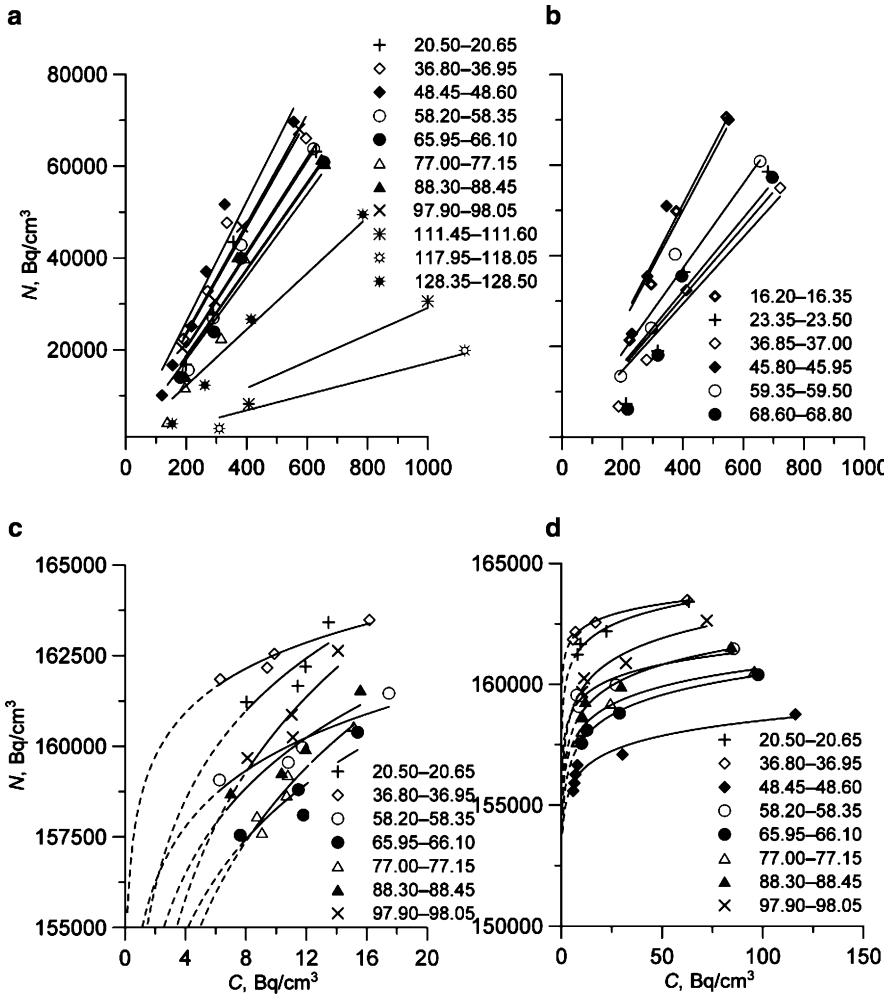


Fig. 22.9 Desorption isotherms. (a), (b) Sr-90: ((a) borehole 01/07, (b) borehole 02/07); (c), (d) Cs-137 and Co-60 (the *full* lines show an analytical approximation of experimental points by isothermal Freundlich relationship, the *dashed* lines are extrapolated curves). Numbers are sampling intervals in the wells (in m)

Table 22.10 Estimated sorption distribution coefficients for Sr-90, cm³/g

Interval, m	K_d^d	K_d^s	Interval, m	K_d^d	K_d^s	Interval, m	K_d^d	K_d^s
Borehole 01/07			Borehole 01/07			Borehole 02/07		
20.50–20.65	46.9	45.6	88.30–88.45	42.8	41.8	16.20–16.35	56.9	59.0
36.80–36.95	54.0	50.4	97.90–98.05	53.1	53.9	23.35–23.50	36.7	39.1
48.45–48.60	59.5	57.1	111.45–111.6	13.3	13.9	36.85–37.00	33.5	34.7
58.20–58.35	46.3	46.7	117.95–118.1	7.8	8.1	45.80–45.95	58.5	57.7
65.95–66.10	42.5	42.3	128.35–128.5	27.8	28.7	59.35–59.50	42.4	42.3
77.00–77.15	40.9	43.2				68.60–68.80	35.2	37.4

and Co-60 show a strong nonlinearity (Fig. 22.9c, d), which manifests itself in low values of the exponential constant ($n^d < 0.1$).

The N - C plots constructed using data of experiments with Cs-137 and Co-60 suggest a very low degree of radionuclide desorption from the mineral: a considerable drop in their concentration in solution has a very weak effect on variations in the concentration on the mineral matrix, which manifests itself in the low values of the exponential constant $n(\equiv n^d)$ and high K_F ($\equiv K_F^d$).

22.7 Diffusion Experiments

Molecular diffusion is the predominant radionuclide-transport mechanism in low-permeability clay formations. Therefore this process was studied in detail using different experimental approaches. The studies included two types of experimental activities: 1D tests with packing clays (disturbed samples) and 1D and 3D tests with undisturbed rock matrix.

22.7.1 *Single-Chamber Diffusion Cell (In/Out-Diffusion) Tests with Packing Cambrian Clay*

Samples of Blue Cambrian clay, taken in Nikol'skii Quarry, were used in diffusion experiments.

22.7.1.1 Experimental Setup

Before the experiments, clay samples were disintegrated to the size of individual aggregates less than 1 mm. The pasted samples were conditioned using SrCl_2 solution of 0.1 N or 3.0 N at room temperature of 20–25 °C. The excessive solution was separated from the solids by centrifuging. These conditioned samples were used in tests carried out under isotonic conditions. To create nonisotonic conditions, pore water was desalted after saturation of the exchange complex of clay with stable strontium (pasted samples were conditioned with distilled water, until chloride ion concentration dropped below 0.001 N).

After conditioning, the pasted samples were thoroughly mixed and placed into chemical columns in small portions with subsequent packing (Fig. 22.10). The height of the clay layer in all experiments was 20–25 cm. Next the column with clay was filled with a stable solution of SrCl_2 with appropriate concentration and exposed for 3–5 days. Just before the diffusion experiments, the solution of stable SrCl_2 was removed from the prepared cylindrical columns, the columns were weighted, and the volume filled by clay was measured.

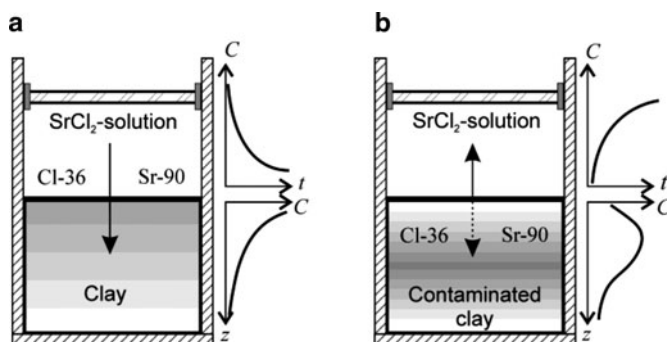


Fig. 22.10 Experimental scheme. (a) Diffusion from solution into sample, (b) diffusion from sample into solution

Radioactive solutions were prepared by adding Cl-36 and Sr-90 isotopes to previously prepared and conditioned solutions of stable SrCl₂ (0.1 and 3.0 N). The volumetric activity of solutions was measured in the process of experiments in 1-ml volumes on a KRK-1 α - β -radiometer with BDIB-01 detector. Unlike Cl-36, the activity of Sr-90 was determined as the difference of two measurements: the total activity of $^{90}\text{Sr} - ^{90}\text{Y}$ and the activity of ^{90}Y . The measurement error at a confidence probability of 95% and the measurement time of 10 s was not more than 3%. The overall error was not more than 10%.

The experiments involved two stages: in-diffusion and out-diffusion.

At the *in-diffusion stage* of the tests, the removed solution was replaced by the initial radioactive solution with known activity, prepared based on stable SrCl₂ in the same concentration as that used to saturate the clay (Fig. 22.10a). The volume of the initial solution was 70 ml. Next, aliquots (each containing 1 ml of radioactive solution) were periodically taken from the middle of water bed above the clay layer and their activity was measured (Fig. 22.11a and 22.12a). The duration of this experimental stage was about 1 month.

At the *out-diffusion stage* of the tests under isotonic conditions, the radioactive solution was replaced by a fresh (isotope-free) solution with the subsequent measurement of accumulated activity in this solution. In each experimental series, the concentration of SrCl₂ in solution corresponded to this salt's concentration in the preconditioned pasted samples. The increase in Cl-36 and Sr-90 concentrations in solution (Fig. 22.11b) is due to their diffusion release from "polluted" samples (Fig. 22.10b).

At the last stage of diffusion experiments, the vertical distribution of residual activity of radionuclides in clay was examined (Figs. 22.9c and 22.10b). At the end of the out-diffusion experiment, the clay core was sliced and the diffusion profile in the clay was determined. The sections were made at the following distances from the top, cm: 0–1, 1–2, 2–3, 3–5, 5–7, 7–12, 12–17, 17–22, and more.

Each clay layer was weighted in wet and dry state, allowing the moisture content distribution along the core length to be determined. Mean radionuclide

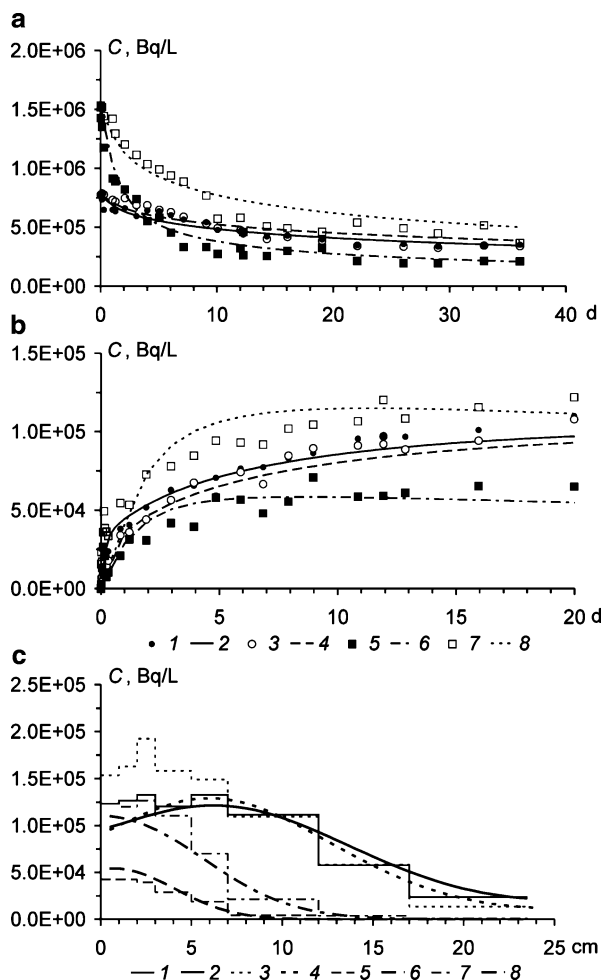


Fig. 22.11 Diffusion experiments under isotonic conditions. (a) In-diffusion stage, $C(t)$, (b) out-diffusion stage, $C(t)$, (c) the distribution of concentration in the pore solution of the sample $C(x)$. (1, 3, 5, 7) Experimental points: (1) Cl-36 (0.1 N SrCl_2), (3) Cl-36 (3.0 N SrCl_2), (5) Sr-90 (0.1 N SrCl_2), (7) Sr-90 (3.0 N SrCl_2); (2, 4, 6, 8) model curves: (2) Cl-36 (0.1 N SrCl_2), (4) Cl-36 (3.0 N SrCl_2), (6) Sr-90 (0.1 N SrCl_2), (8) Sr-90 (3.0 N SrCl_2)

concentration was measured in each dried clay sample. The activity in the samples was measured on a KRK-1 radiometer (the sensitivity threshold was $1 \cdot 10^{-6}$ Ci/kg dry mass) or on a shielded α - β -radiometer UMF-2000 (the same sensitivity threshold). The measurements were made in three parallel samples from each layer with 3–5 measurements in each sample with the aim to reduce the overall error in determining the activity of the preparation to not more than 30%. Figures 22.11c and 22.12b also give the concentrations in pore water obtained after recalculating the weight concentrations via the effective porosity (see below).

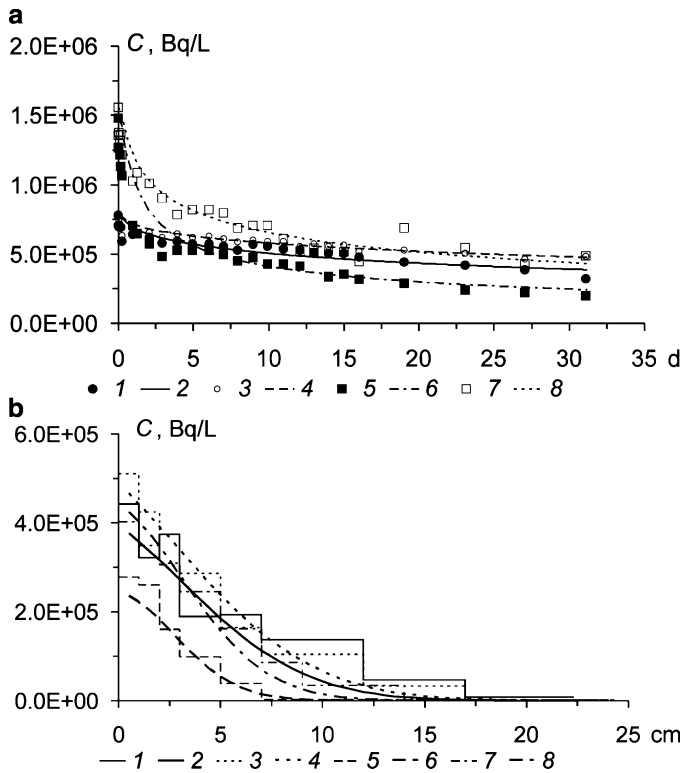


Fig. 22.12 Diffusion experiments under nonisotonic conditions. (a) “Direct” diffusion $C(t)$, (b) concentration distribution in the pore solution of the sample $C(x)$. The notations see in Fig. 22.9

22.7.1.2 Breakthrough Curve Interpretations

The first stage of parameter identifications was based on the measurement of the concentration decrease in the injection chamber. The process can be described by a partial solution of the one-dimensional differential equation

$$R \frac{\partial C}{\partial t} - D_m \frac{\partial^2 C}{\partial x^2} = 0, \quad (22.1)$$

combined with the condition of isotope balance in a limited volume of solution in the chamber

$$h \frac{\partial C}{\partial t} = -\phi D_m \left. \frac{\partial C}{\partial x} \right|_{x=0}. \quad (22.2)$$

This solution, written for the concentration function in the chamber $C \equiv C(x = 0, t)$ under the conditions $C(x, t = 0) = C_0, C(x \rightarrow \infty, t) = 0$, can be represented as (Crank 1975; Van Rees et al. 1991; Moridis 1999; Giu et al. 2009)

$$\bar{C} = \exp(a^2 t) \operatorname{erfc}(a \sqrt{t}), \quad (22.3)$$

where $a = \phi \sqrt{D_m R}/h$, $\bar{C} = C/C_0$, C_0 is the initial concentration in the chamber, D_m is the pore diffusion coefficient, ϕ is the porosity, h is the thickness of the solution layer in the chamber, $R = 1 + K_d \rho_b / \phi$ is the retardation factor.

Unfortunately, as mentioned above, the processing of the experimental breakthrough curve, characterizing the drop in concentration in the registration chamber, gives little information, since only a value for the combination $\phi^2 R D_m^{\text{in}}$ can be obtained. The interpretation potential radically increases in the presence of data on the spatial distribution of indicators (both adsorbed and inert) in the pore space, $C = C(x, t)$, and the record of function $C^{\text{out}} \equiv C(0, t > t_0)$, obtained in the period of their reverse diffusion from the sample into solution (in the case of change in its composition at some moment $C^{\text{out}} = (0, t = t_0) = 0$); here, t_0 is the duration of diffusion into the sample. In this case, the solution of the problem for heterogeneous initial conditions can be obtained numerically.

22.7.1.3 Tests Under Isotonic Conditions

The major experimental characteristics are given in Table 22.11 along with the balance of isotope activities. It is worth mentioning that the observed disbalance in

Table 22.11 Laboratory series and experimental parameters (isotonic conditions)

Test parameters ^a		Isotopes and solutions			
		Cl-36		Sr-90	
		0.1 N SrCl ₂	3.0 N SrCl ₂	0.1 N SrCl ₂	3.0 N SrCl ₂
In	C_0 , Bq/L	$7.77 \cdot 10^5$	$7.77 \cdot 10^5$	$1.52 \cdot 10^6$	$1.52 \cdot 10^6$
	F_c , cm ²	16.6	19.0	17.0	20.0
	L_c , cm	23.5	24.0	22.0	23.5
	ρ_{bwet} , g/cm ³	1.65	1.69	1.67	1.68
	ρ_{bdry} , g/cm ³	1.02	1.05	1.02	1.05
	V_i , ml	70	70	70	70
	V_f , ml	45.8	45.8	44.6	43.6
	h , cm	3.64	3.15	3.83	3.06
	V_i , ml	98.0	98.0	98.0	68.5
	V_f , ml	69.2	70.4	68.0	39.7
Out	h , cm	5.00	4.39	5.07	2.81
	A_{in}^L , Bq	$2.61 \cdot 10^4$	$2.61 \cdot 10^4$	$8.53 \cdot 10^4$	$7.05 \cdot 10^4$
	A_{out}^L , Bq	$9.14 \cdot 10^3$	$9.01 \cdot 10^3$	$5.61 \cdot 10^3$	$6.85 \cdot 10^3$
Balance	$A_{\text{in}}^L - A_{\text{out}}^L$, Bq	$1.70 \cdot 10^4$	$1.71 \cdot 10^4$	$7.97 \cdot 10^4$	$6.36 \cdot 10^4$
	A^s , Bq	$2.65 \cdot 10^4$	$2.60 \cdot 10^4$	$9.10 \cdot 10^4$	$6.61 \cdot 10^4$
	$\alpha = \frac{A_{\text{in}}^L - A_{\text{out}}^L}{A^s}$	0.642	0.660	0.875	0.963

^aHere and in Table 22.13: F_c is column cross-section area; L_c is column length; ρ_{bwet} is wet-rock density; ρ_{bdry} is dry-rock density; V_i is the initial chamber volume; V_f is the final chamber volume; h is the mean chamber height; A_{in}^L is the decrease in isotope activity in the chamber; A_{out}^L is the accumulated activity of isotope in the chamber; A^s is isotope activity in the column; *in* refers to diffusion from solution into the column, and *out*, to diffusion from the column (sediment) into solution.

the experiment is due to the isotope activity in the liquid and solid phases having been measured under different conditions. Therefore, in further calculations, the concentrations in solid phase were corrected by multiplying the measured values by a correction factor α . We emphasize that in the moment of measurement, the solid phase was represented by dried clay (with a density of ρ_{bdry}); thus, such measurement reflected the total concentration of isotopes in pore solution and on mineral matrix.

In the model analysis of experimental results, the measured isotope concentrations (activities) in solid phase were converted into concentrations in pore solution by the formula $C = C^s \rho_{bdry} \alpha / \phi R$, where C^s is the measured activity in the clay, and parameter R^{out} (the effective porosity at the stage of diffusion from the column) was fitted in the course of modeling.

The initial stage of interpretation of experiments was based on the solution of equation (22.3), which was used to fit the coefficient a and evaluate the aggregate parameter $\phi^2 D_m R^{in} = (\phi R^{in})^2 D_a$ (Table 22.12), where D_m is the pore diffusion

Table 22.12 Calculated (model) parameters of diffusion and sorption (desorption) distribution (isotonic conditions)

		Isotopes and solutions			
		Cl-36		Sr-90	
Test parameters		0.1 N SrCl ₂	3.0 N SrCl ₂	0.1 N SrCl ₂	3.0 N SrCl ₂
$a, d^{-1/2}$		0.153	0.145	0.616	0.278
$\phi^2 D_m R^{in}, m^2/c$		$5.60 \cdot 10^{-10}$	$2.43 \cdot 10^{-10}$	$6.44 \cdot 10^{-9}$	$8.39 \cdot 10^{-10}$
$D_m, m^2/c$		$1.3 \cdot 10^{-9}$	$9.7 \cdot 10^{-10}$	$1.7 \cdot 10^{-9}$	$9.9 \cdot 10^{-10}$
$D_a, m^2/c$		$1.2 \cdot 10^{-9}$	$9.7 \cdot 10^{-10}$	$1.1 \cdot 10^{-10}$	$2.9 \cdot 10^{-10}$
R	In	1.1	1.0	15.0	3.4
	Out	1.1	1.0	39.0	9.0
$K_d, cm^3/g$	In	≈ 0.03	0.0	4.19	0.71
	Out	≈ 0.03	0.0	11.38	2.38

Table 22.13 Laboratory series and experimental parameters (nonisotonic conditions)

	Isotopes and solutions			
	Cl-36		Sr-90	
Test parameters	0.1 N SrCl ₂	3.0 N SrCl ₂	0.1 N SrCl ₂	3.0 N SrCl ₂
C ₀ , Bq/L	7.77 · 10 ⁵	7.77 · 10 ⁵	1.48 · 10 ⁶	1.55 · 10 ⁶
F _c , cm ²	18.25	16.21	18.44	17.23
L _c , cm	22.3	24.0	24.3	23.5
ρ _{b wet} , g/cm ³	1.58	1.62	1.55	1.59
ρ _{b dry} , g/cm ³	1.02	1.05	1.02	1.05
V _i , ml	98	98	98	98
V _f , ml	68	68	68	67
h, cm	4.55	5.12	4.50	4.79
Balance	A ^L _{in} , Bq	1.02 · 10 ⁻⁶	6.88 · 10 ⁻⁷	3.11 · 10 ⁻⁶
	A ^s , Bq	1.36 · 10 ⁻⁶	1.05 · 10 ⁻⁶	4.33 · 10 ⁻⁶
	α = $\frac{A_{in}^L}{A^s}$	0.756	0.656	0.718
				0.788

coefficient and $D_a = D_m/R^{\text{in}}$ is the apparent diffusion coefficient. Next, the model was used to fit $D_m(D_a)$, R^{in} , and R^{out} (retardation factors) based on the breakthrough concentration functions $C^{\text{out}}(0, t)$, obtained in the in-diffusion tests, and data on the isotope distributions in rock sediment $C(x, t_k)$, where t_k is the final time. As can be seen from the resulting plots in Fig. 22.11, the model adequately reproduces the experimental curves.

The obtained values of molecular diffusion coefficients for chloride and strontium ions were found to be close to one another: in the solution with a low ionic strength, $D_m = (1.3\text{--}1.7) \cdot 10^{-9} \text{ m}^2/\text{c}$, while in the concentrated solution $D_m = (9.7\text{--}9.9) \cdot 10^{-10} \text{ m}^2/\text{d}$, i.e., the diffusion coefficient decreases by a factor of about one and a half. The values of effective porosity, established for chloride ions, are close to the total clay porosity ($\phi^0 \approx 0.6$). Hereafter, we assume $\phi = 0.5$. The experiments revealed appreciable sorption of Sr-90, which was maximal in pore waters with low ionic strength (0.1 N): the appropriate coefficient of sorption distribution $K_d = 4.2 \text{ cm}^3/\text{g}$ is 6 times as large as K_d ($0.7 \text{ cm}^3/\text{g}$), evaluated for a concentrated (3.0 N) solution.

It is important to note that the processing of the results of experiments with radiostrontium yielded a considerable difference between the calculated (fitted) values of R for the stages of diffusion from solution into the sample (R^{in}), when adsorption of this radionuclide takes place, and for the stage of diffusion from this sample (R^{out}), when desorption takes place: $R^{\text{out}} \gg R^{\text{in}}$. The calculated values of K_d were about 11.4 and $2.4 \text{ cm}^3/\text{g}$ (in the clay saturated with low-salinity and concentrated solutions, respectively).

22.7.1.4 Tests Under Nonisotonic Conditions

These experiments were restricted to the “direct diffusion” stage (Table 22.13). As well as in the processing of the previous experimental series, at the first stage, the analytical relationship (22.3) was used to evaluate the aggregate parameter $\phi^2 D_m R^{\text{in}} = (\phi R^{\text{in}})^2 D_a$, and next the numerical model was used to separately fit the parameters $D_m(D_a)$ and $R \equiv R^{\text{in}}$ (Table 22.14) for the best approximation of experimental data (Fig. 22.12).

Table 22.14 Calculated (model) parameters of diffusion and sorption distribution (nonisotonic conditions)

Test parameters	Isotopes and solutions			
	Cl-36		Sr-90	
	0.1 N SrCl ₂	3.0 N SrCl ₂	0.1 N SrCl ₂	3.0 N SrCl ₂
$a, \text{d}^{-1/2}$	0.12	0.09	0.60	0.32
$\phi^2 D_m R^{\text{in}}, \text{m}^2/\text{c}$	$4.69 \cdot 10^{-10}$	$2.45 \cdot 10^{-10}$	$8.44 \cdot 10^{-9}$	$2.75 \cdot 10^{-9}$
$D_m, \text{m}^2/\text{c}$	$1.0 \cdot 10^{-9}$	$8.2 \cdot 10^{-10}$	$2.4 \cdot 10^{-9}$	$1.8 \cdot 10^{-9}$
$D_a, \text{m}^2/\text{c}$	$5.5 \cdot 10^{-10}$	$6.8 \cdot 10^{-10}$	$1.7 \cdot 10^{-10}$	$3.0 \cdot 10^{-10}$
R (in)	1.8	1.2	14	6
$K_d, \text{cm}^3/\text{g}$ (in)	≈ 0.25	≈ 0.06	4.19	1.57

Overall, the coefficients of molecular diffusion obtained in experiments under nonisotonic conditions are very close to the values given before. The most significant deviation (by one and a half to two times toward greater values) was recorded for Sr-90. The coefficients of equilibrium sorption distribution of Sr-90 under different conditions are also similar. We should also mention the low sorption capacity of rock with respect to chloride isotopes (relative to the previous experimental series, where the sorption of this component was negligible).

22.7.1.5 Conclusions

The results of analytical and numerical (model) interpretation of laboratory experiments with Blue Cambrian clay allow us to come to the following generalizations.

1. The use of radioactive tracers allows one to study the diffusion of individual ions not complicated by osmotic and electrical-kinetic processes.
2. Under isotonic conditions, when the chemistry of solutions is the same, the diffusion capacity of chloride and strontium ions is similar.
3. The dependence of self-diffusion coefficients on solution concentration is determined: under isotonic conditions, the estimated coefficient of molecular diffusion decreases about two times with increasing ionic strength, while, under nonisotonic conditions, this tendency is less pronounced.
4. An increase in the ionic strength of solution leads to a decrease in the sorption capacity; the appropriate estimates of the sorption distribution coefficient K_d are $4.2 \text{ cm}^3/\text{g}$ (0.1 N SrCl_2 solution) and $0.7 \text{ cm}^3/\text{g}$ ($1.57 \text{ cm}^3/\text{g}$ for nonisotonic conditions) (3.0 N SrCl_2 solution).
5. The obtained results suggest the manifestation of sorption hysteresis: the coefficients of sorption distribution during the diffusion of ions from the sample into solution (when the ions that have been adsorbed before are being desorbed) are much (3–4 times) greater than the respective values obtained for the stage of diffusion from solution into the sample.
6. Because of experimental errors, the agreement between the experimental and model curves is far from ideal. Therefore, the errors in the estimates of migration parameters can be as large as 20–30%.

22.7.2 *Single-Chamber Diffusion Cell Tests with Undisturbed Vendian Clay Samples*

In this experimental set-up samples for single-chamber diffusion cells (Fig. 22.10a) were cut from the borehole core material without its crushing. Samples of cylindrical-shape (ranges in length from 3 to 5 cm and 5 cm in diameter) were drilled out using special core-drilling bit. For each experimental series with HTO (tritiated water), Sr-90, Cs-137 and Co-60 several pairs of the cylindrical-shape

Table 22.15 Results of interpretation of single-chamber diffusion cell tests with undisturbed clay samples

Code of sample ^a	$a, d^{-1/2}$ ^b	$D_m \phi^2 R \times 10^9, \text{ m}^2/\text{s}$ ^c	Code of sample	$a, d^{-1/2}$	$D_m \phi^2 R \times 10^9, \text{ m}^2/\text{s}$
Sr-90					
4/10-17(∥)	0.3	3.88	4/10-65(⊥)	0.25	2.70
4/10-17(⊥)	0.2	1.73	4/10-68(∥)	0.55	13.1
4/10-37(∥)	1.1	52.0	4/10-68(⊥)	0.3	3.88
4/10-37(⊥)	0.16	1.11	4/10-80(∥)	0.55	13.1
4/10-53(∥)	0.3	3.88	4/10-80(⊥)	0.2	1.73
4/10-53(⊥)	0.3	3.88	4/10-35(⊥)	0.7	21.1
4/10-65(∥)	0.13	0.73	4/10-83(⊥)	0.4	6.91
HTO					
4/10-37(∥)	0.077	0.18	4/10-80(∥)	0.05	0.075
4/10-37(⊥)	0.043	0.056	4/10-80(⊥)	0.03	0.027
4/10-68(∥)	0.056	0.094	4/10-80(∥)	0.045	0.061
4/10-68(⊥)	0.035	0.037	4/10-80(⊥)	0.06	0.11

^aFirst number corresponds to borehole number (Sect. 22.1), depth (in m) of sampled interval follows after hyphen, (∥) is a sign for a diffusion test parallel to bedding planes; (⊥) the same for a diffusion test perpendicular to bedding planes

^bAs in solution (22.3)

^cFor $h = 6.11$ cm (Sr-90) and $h = 5.1$ cm (HTO)

samples were prepared. Each pair of the samples characterized a certain depth of the Vkt formation (Table 22.15). One of the each pair of samples was drilled out in such a way that its axis was directed parallel to bedding planes. The other pair-sample was reoriented towards a direction that is perpendicular to bedding planes.

The laboratory diffusion experiments were analyzed following the presented above mathematical model (22.1)–(22.3). The selected experimental set-up and sampling technique allow us to determine the values of the combined parameter, $D_m \phi^2 R$, reflecting radionuclide diffusion and retention parallel and perpendicular to clay bedding planes, in different intervals of the studied cross-section. Typical breakthrough curves for experiments with Sr-90 and HTO are presented in Fig. 22.13, Table 22.15 summarizes interpretation of the experimental data.

Results of experiments with Sr-90 demonstrate that combined parameter, $D_m \phi^2 R$, varies widely over depth that can be explained by the changes in lithologic composition and mineralogy of the strata, and variability in clay to silt-sand particle ratio. The HTO behavior is less dependable on depth. Obviously micro-layered character of the rock is responsible for the measured apparent diffusion anisotropy (Fig. 22.14): calculated values of $D_a(\parallel)/D_a(\perp)$ ratio exceed (with one exception) 1. Anisotropy ratio for H-3, $D_m(\parallel)/D_m(\perp)$, ranges within 2.5 to 3.3. The obtained values of the pore diffusion coefficient for HTO, D_m , vary between $6.8 \cdot 10^{-10}$ and $4.5 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

Unfortunately, the experiments with two other radionuclides, Cs-137 and Co-60, could not be successively interpreted in the frameworks of model (22.1)–(22.3).

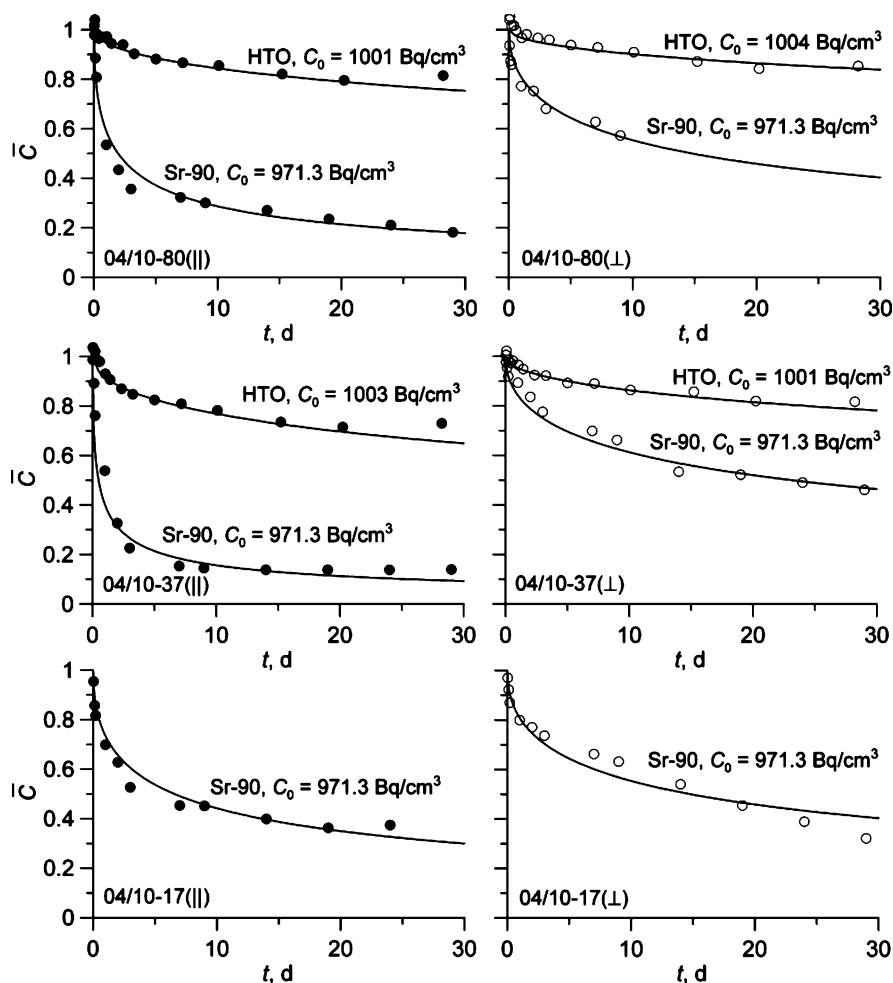
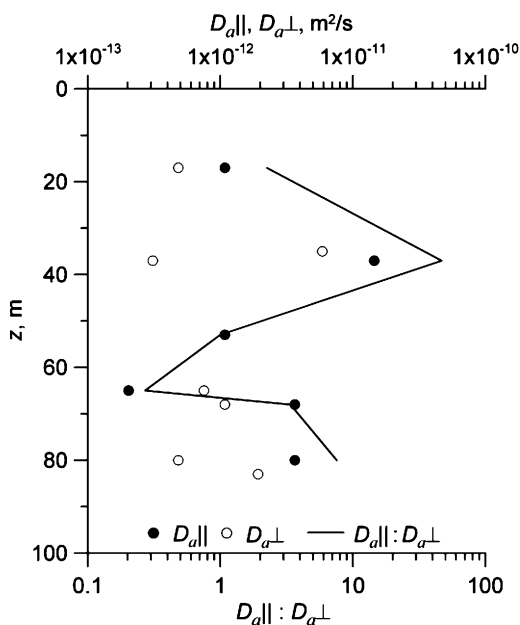


Fig. 22.13 Breakthrough curves for Sr-90 and HTO diffusion-in experiments with understurbed samples

Selected experimental time for these strongly adsorbable species was too short to allow them to diffuse inside the core samples more than in a few tens to a few hundreds of micrometers from the liquid/solid surface interface, and observed decrease in concentration of Cs-137 and Co-60 in the injection chamber was connected mostly with sorption kinetics on this interface. In general, it seems that single-chamber experimental set-up is not appropriate option for studying diffusion and retention of strongly adsorbable radionuclides: the sensitivity of the breakthrough curves to the diffusion process is very low in comparison to the surface sorption kinetics.

Fig. 22.14 Longitudinal (parallel to bedding planes) and transverse (perpendicular to bedding planes) apparent diffusion coefficients for Sr-90 versus depth (from the data in Table 22.15, assuming $R = 299.5$, $\phi = 0.2$). Factor R was calculated assuming $K_d = 30 \text{ cm}^3/\text{g}$, $\rho_b = 1.99 \text{ g/cm}^3$



22.7.3 A 3D Diffusion Test with a Cambrian Clay Sample of Natural Structure

In this section, we give the results of experimental studies of diffusion transport of radionuclides in a block sample of a rock that has a *microlayered structure*. This type of rock heterogeneity can lead to different values of molecular diffusion coefficient in different directions – along and across bedding planes. This is a manifestation of anisotropy in clay properties for this mass transport mechanism. The block sample was taken at a depth of 30 m from the roof of clays at the lower bench of Nikol'skii Quarry (Leningrad province), which strips Blue Cambrian clay.

22.7.3.1 Experimental Setting

The dimensions of the sample were $46 \times 20 \times 28 \text{ cm}$. The duration of experiment was 17 months (510 days). To preserve the natural moisture content, the sample was paraffined according to a standard procedure (Fig. 22.15a). A hole 4.2 cm in depth was drilled at the flat end of the sample (Fig. 22.15b) and filled by a radioactive “cocktail” of radionuclides Cl-36, Sr-90, Cs-137 and Co-60 (Table 22.16).

The hole was sealed by clay powder and the exposed surface was sealed by paraffin. Considering the small volume of the introduced liquid, we can assume that the experiment was carried out at constant moisture content. To minimize the external impact, the container with clay sample was stored in a basement room at constant

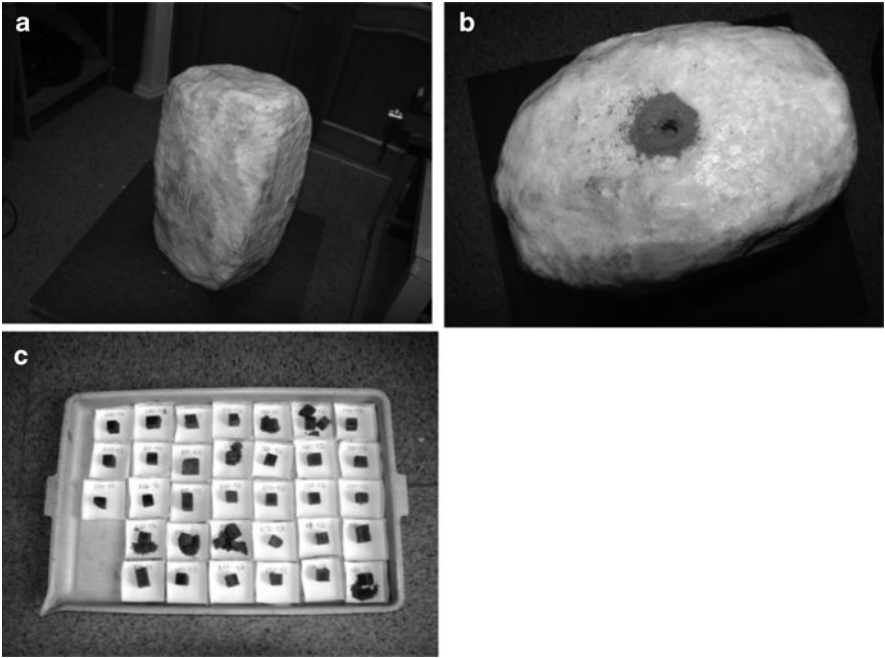


Fig. 22.15 (a) A sample of clay in protected paraffin coating, (b) a hole for radionuclide cocktail injection, and (c) rectangular samples of clayey material prepared for isotope detection

Table 22.16 Characteristic of the concentration source

Radionuclide	Activity (Bq) ^a
Cl-36	$1.68 \cdot 10^{+6}$
Sr-90	$3.70 \cdot 10^{+5}$
Cs-137	$5.14 \cdot 10^{+5}$
Co-60	$3.43 \cdot 10^{+5}$

^aThe activities of radionuclides 2.5 ml in volume in the sample

temperature (10°C). After the exposition, the block sample was taken from the container, divided into layers 4 cm in height perpendicular to the direction of the drilled hole. After marking each layer, it was cut into cubes with a side of 2 cm (Fig. 22.15c).

Immediately after cutting, the cubes were dried until constant mass at $T = 105^{\circ}\text{C}$ and homogenized into powder. The clay sample treated in this manner was placed on measuring backings with appropriate shape, on which the composition and specific activity of radionuclides in individual disintegrated cubes were determined by β - and γ -spectrometry. The measured weight concentrations (activities) obviously reflect the total concentrations of radionuclides in pore solution and on the mineral matrix at the moment when sample drying started.

22.7.3.2 Mathematical Model of the Test

Diffusion of a stable nonreactive component in an anisotropic porous medium is described by Eq. 1.17. The migration of a sorbable unstable component can be described by the following equation:

$$R \frac{\partial C}{\partial t} - D_{mT} \frac{\partial^2 C}{\partial x^2} - D_{mL} \frac{\partial^2 C}{\partial y^2} - D_{mL} \frac{\partial^2 C}{\partial z^2} + \lambda CR = 0, \quad (22.4)$$

where D_{mL} and D_{mT} are the principal components of the orthotropic pore diffusion tensor (1.18), parallel to the bedding and perpendicular to the bedding, respectively; C is the concentration (activity) of the radionuclide in solution [Bq/cm³].

As applied to a stratified system, the equation (22.4) is effective, since the phenomena induced by a "rhythmic" heterogeneity of the medium are described by it in an indirect manner by incorporating generalized parameters D_{mT} and D_{mL} in the model. However, when the averaging of the process is not sufficient, scale effects may appear. These effects are due to the fact that the part of the medium involved in the process within the experiment time includes a limited number of heterogeneity elements (layers).

Of interest for us is the solution of equation (22.4) with the following boundary conditions:

$$C(x \rightarrow \infty, y, z, t) = 0, C(x, y \rightarrow \infty, z, t) = 0, C(x, y, z \rightarrow \infty, t) = 0, \quad (22.5a)$$

$$C_i(x, y, z, 0) = \frac{M}{nR} \delta(x, y, z); \quad (22.5b)$$

here $\delta(x, y, z)$ is Dirac delta function [cm⁻³], M is the activity of the radionuclide that entered the porous medium in point $x = 0$, $y = 0$, $z = 0$ at moment $t = 0$ [Bq].

The exact solution of equation (22.4) with boundary conditions (22.5a) has the form (Ogata and Banks 1961):

$$C(x, y, z, t) = \frac{M}{8\phi\sqrt{\pi^3 t^3 D_{aT} D_{aL} D_{aL}}} \cdot \exp \left[-\frac{x^2}{4D_{aT}t} - \frac{y^2}{4D_{aL}t} - \frac{z^2}{4D_{aL}t} - \lambda t \right], \quad (22.6)$$

where $D_a = D_m/R$ is the apparent diffusion coefficient [cm²d⁻¹] (Sect. 1.1.2); x , y , z are the distances from of the source along coordinate axes [cm]. The dimensions used here assume that the volumetric activity of radionuclides in solution is measured in Bq/cm³.

As mentioned above, the activity of radionuclides measured in a clay charge is associated with the total (both in pore water and rock exchange complex) activity of radionuclides converted to unit rock mass ΣC_g (Bq/g). Given the density ρ_b , the volumetric activity becomes $\Sigma C = \rho_b \Sigma C_g$ (Bq/cm³). Therefore, the adaptation of the calculation scheme to the above measurement procedure can be described by the equation

$$\Sigma C = \phi C + N = \phi RC, \quad (22.7)$$

where ΣC is the total activity of the radionuclide in a unit rock volume [Bq/cm^3]; C is radionuclide activity in pore water [$\text{Bq}/\text{cm}^3_{\text{liquid}}$]; $N = K_d \rho_b C$ is the activity on the rock [$\text{Bq}/\text{cm}^3_{\text{solid}}$].

We rewrite equation (22.6) for the total activity function (22.7), with the assumption that the matter source is located near an impermeable (reflecting) boundary

$$\sum C(x, y, z, t) = \frac{MR}{4\sqrt{\pi^3 t^3 D_{aL}^3/\chi}} \cdot \exp \left[-\frac{\chi x^2 + y^2 + z^2}{4D_{aL}t} - \lambda t \right]. \quad (22.8)$$

where $\chi = D_{aL}/D_{aT} > 1$ is the anisotropy coefficient for parameter D_a .

In principal, Eq. 22.8 can be used directly to calculate the 3D concentration profiles for different values of the parallel and perpendicular diffusion coefficients in the tests. These theoretical profiles can be compared with the experimental results in order to identify which values of the diffusion coefficients provided the best fitting of the experimental results. An alternative approach is based on linearization of Eq. 22.8. Taking the logarithms of the left and right parts of solution (22.8), we obtain its linearized representation:

$$\ln \left(\sum C(x, y, z, t) \right) = G - B(\chi \cdot x^2 + y^2 + z^2), \quad (22.9)$$

where

$$B = \frac{1}{4D_{aL}t} \text{ and } G = \ln \left(\frac{MR}{4\sqrt{\pi^3 t^3 D_{aL}^3/\chi}} \right) - \lambda t. \quad (22.10)$$

Equation 22.9 is linear in coordinates $\ln(\Sigma C) \div (\chi \cdot x^2 + y^2 + z^2)$. Therefore, it makes sense in the quantitative analysis of experimental material to use the following procedure:

1. to fit the value of the anisotropy coefficient χ , such that the experimental data are best (with the least scatter, i.e., minimal mean-square deviation) approximated by the straight line (22.9);
2. to evaluate the slope of this line, i.e., the coefficient B , and the shift G ;
3. to evaluate the apparent diffusion coefficient D_{aL} from the slope B using the formula $D_{aL} = 1/4Bt$;
4. to evaluate the second component of the diffusion coefficient: $D_{aT} = D_{aL}/\chi$;
5. to use D_{aL} and G to calculate the retention factor: $R = (4 \exp(G + \lambda t)/M) \times \sqrt{\pi^3 t^3 D_{aL}^3/\chi}$;
6. to evaluate diffusion coefficients for each direction: $D_{mL} = D_{aL}R$, $D_{mT} = D_{aT}R$.

Since measurements of Cs-137 and Co-60 concentrations show considerable scatter, we will focus our further analysis on interpretation of measurements of 3D distribution of Cl-36 and Sr-90 within the clayey block.

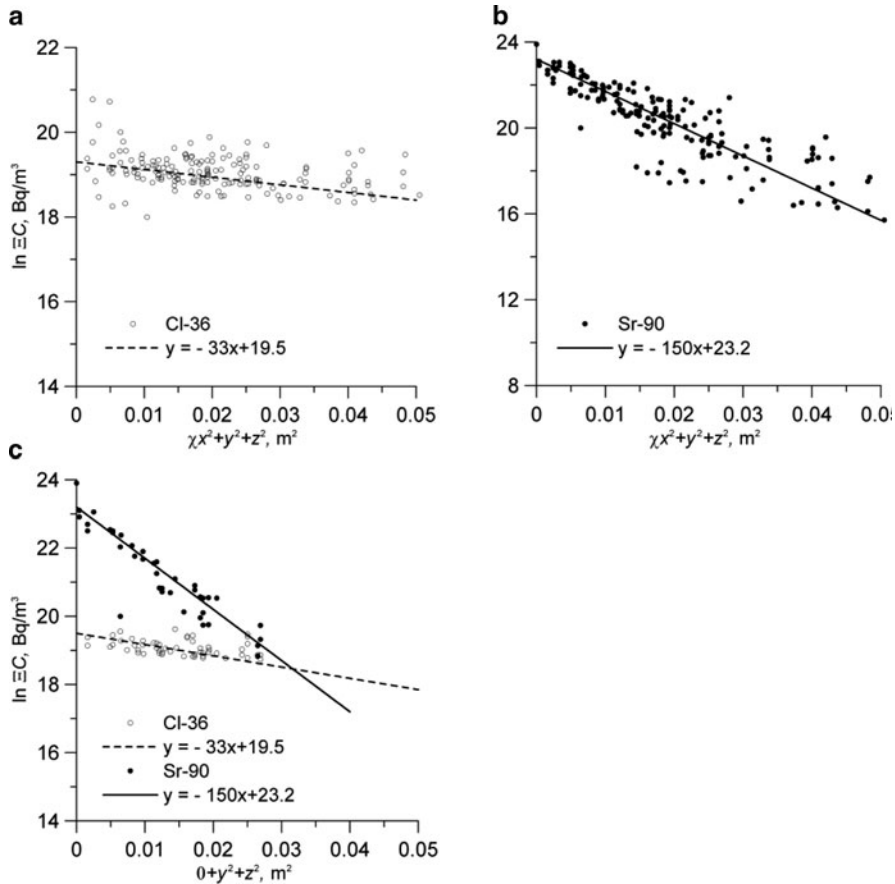


Fig. 22.16 Linearization of experimental data. (a) Cl-36: complete sample of points $C(x, y, z)$ with fitting the anisotropy coefficient χ ; (b) Sr-90: complete set of points $C(x, y, z)$ with fitting the anisotropy coefficient χ ; (c) set of points along the bedding plane (Y-Z plane)

22.7.3.3 Results of Test Data Interpretation

Figure 22.16 gives the results of interpretation of experimental data for Cl-36 and Sr-90, which was carried out in accordance with the above scheme. Each calculation variant is illustrated by (a) the complete set of samples with the approximating solution line (22.9) and the fitted anisotropy coefficient, χ ; (b) a set of points that characterizes the radionuclide concentration distribution in the main plane (0, Y, Z). The construction of the plot 22.16, c was required for minimizing the effect on the accuracy of evaluation of averaged parameters caused by the distribution of experimental points in different lithological layers (see below).

The best agreement of experimental and calculated concentration distributions with Eq. 22.8 was obtained as shown in Table 22.17. It is seen that the tested

Table 22.17 Summary table of the values of apparent diffusion coefficients $D_a = D_m/R$ (m^2/c)

Radionuclide	B	G	D_{aL}	D_{aT}	R	D_{eL}	D_{eT}	χ
Cl-36	18	19.3	$1.7 \cdot 10^{-10}$	$2.9 \cdot 10^{-11}$	1.05	$3.7 \cdot 10^{-11}$	$6.4 \cdot 10^{-12}$	5.8
Sr-90	150	23.2	$3.8 \cdot 10^{-11}$	$6.3 \cdot 10^{-12}$	20.6 ^a	$1.6 \cdot 10^{-10}$	$2.7 \cdot 10^{-11}$	6

^a $K_d \approx 2 \text{ cm}^3/\text{g}$ (for $\phi = 0.21$ and $\rho_b = 2.1 \text{ g/cm}^3$)

sample clay exhibits fairly strong diffusion anisotropy due to stratification, and, as could be expected, $D_{aL} > D_{aT}$, that coincides with experiments discussed in Sect. 22.7.2. Moreover, it can be seen that the appropriate values form the series: Cl-36 > Sr-90. By the degree of their sorption, the radionuclides form another series: Sr-90 > Cl-36.

At the same time, the scatter of values around the theoretical line (22.9) is quite significant. This is due to the lithological heterogeneity (stratification) of the sample, i.e., by the alternation of layers (mm-scale heterogeneity) with different clay material content: a sampling point lying in a clay seam yields extremely high radionuclide activity, corresponding to its adsorbed state, while the sampling of an adjacent silt/sand-enriched layer yields lower activity.

For Cs-137 and Co-60, which are the most sorbed radionuclides, this effect proved to be critical, since the localization of these radionuclides near the concentration source prevented the reaching of the required averaging level of the properties of clayey rock with microlayer structure.

Overall, the experiment is unique in some sense, since it simulates the three-dimensional migration of radionuclides in a rock sample with natural structure under nearly real conditions. The effective parameters of diffusion and sorption coefficients obtained for different radionuclides make it possible to simulate their migration in clay strata in assessing the safety of construction of underground repository for RW disposal.

22.7.4 A Comparative Analysis

Tables 22.18 and 22.19 summarize the published results of laboratory tests with undisturbed clay samples taken from clay formations considered as potential host rocks for the underground repository for RW disposal in the Western Europe. Analyzing these results as well as results obtained in the discussed above experiments with Vkt and CBlue clays one may come to the conclusions as follows.

1. Because of anion exclusion effects (Van Loon et al. 2003), anions (such as $^{36}\text{Cl}^-$ and $^{125}\text{I}^-$) diffuse slower and exhibit smaller diffusion-accessible porosities, ϕ , than the uncharged HTO: the values of the effective diffusion coefficient of HTO are 3–10 times higher than those of $^{36}\text{Cl}^-$ and $^{125}\text{I}^-$ (Table 22.18).
2. Similar values of D_e for the studied neutral and anionic radionuclides were measured in both OPA and COx clays. These values are 3–4 times smaller than the values of effective diffusion coefficients obtained for less consolidated Boom clay (BC), Table 22.18.

Table 22.18 Effective diffusion coefficients, D_{eT} (m^2/s), for conservative (non-sorbed) tracers obtained in laboratory experiments with BC, Cox, and OPA, *undisturbed* clay samples

Index	BC (Mol)	Cox (Bure)			OPA (Mont Terri)		
Ref	[1]	[2] ^a	[3]	[4] ^b	[5]	[4] ^b	[6] ^b
HTO, 10^{-11}	8.5	2.6	1.8–4.2	6–9	1.2–1.5	4–8	1.5
ϕ	0.37	0.18	0.15	0.16	0.1	0.16	0.15
$^{36}\text{Cl}^-$, 10^{-12}	24	5.8	4.4–8.9		4.1–5.7		1.0
ϕ	0.16	0.09			0.07		0.08
$^{125}\text{I}^-$, 10^{-12}	22	2.8			3.4–4.8		
ϕ	0.16	0.13			0.08–0.11		

^aCoefficient D_{eT} calculated using D_{eL} data from through-diffusion laboratory experiments, $\chi = 1.56$

^bLarge scale laboratory experiment, $\chi = 3\text{--}4$

References: [1] Aertsens et al. 2008; [2] Samper et al. 2008; [3] García-Gutiérrez et al. 2008; [4] Cormenzana et al. 2008; [5] Van Loon et al. 2003; [6] García-Gutiérrez et al. 2006; [7] Van Loon et al. 2005; [8] Maes et al. 2009; [9] Wersin et al. 2008

Table 22.19 Apparent diffusion coefficients, D_{aT} (m^2/s), for Sr-90 (89) obtained in laboratory experiments with BC, Cox, and OPA *undisturbed* clay samples

Index	BC (Mol)	Cox (Bure)		OPA (Mont Terri)		
Ref	[8] ^a	[3] ^a	[3,4] ^b	[7] ^a	[4] ^b	[9] ^c
D_{aT} , 10^{-12}	7.8 ± 1.5	7.06 ± 0.26	0.6–2	7.4–8.5	1–3	22
ϕ	0.37	0.15		0.09–0.11		0.17
K_d , cm^3/g	257	0.87 ± 0.45		0.64–0.75		1.4
ρ_b , g/cm^3	1.7 (dry)	2.4		~ 2.0		~ 2.0
R	1182	14.9		17–22		17.5

^aSmall-scale laboratory experiment

^bLarge-scale laboratory experiment, D_{aL} value

^cSmall-scale laboratory experiment, D_{aL} value

References: [3] García-Gutiérrez et al. 2008; [4] Cormenzana et al. 2008; [7] Van Loon et al. 2005; [8] Maes et al. 2009; [9] Wersin et al. 2008

- Diffusion coefficients are larger in the direction parallel to the bedding plane than perpendicular to it.
- The values of effective diffusion coefficients D_{eL} and D_{eT} for $^{36}\text{Cl}^-$ obtained in the 3D laboratory experiment with CBlue clay (Table 22.17) are similar to those obtained in OPA and COx clays (Table 22.18).
- In situ diffusion experiments (carried out at Mont Terri, OPA clay) with non-sorbable tracers (HTO, HDO, $^{36}\text{Cl}^-$ and $^{125}\text{I}^-$) confirmed, in general, all tendencies established under laboratory conditions (Palut et al. 2003; Yllera et al. 2004; Samper et al. 2006; Soler et al. 2008). In particular, the field effective diffusion coefficients, D_{eL} and D_{eT} , predominantly fall within the average range of values found in laboratory tests. The anisotropy factor $\chi = D_{eL}/D_{eT}$ varies within the average range from 2 to 6.
- The comparison of the D_{aT} value for Sr-90 obtained in the 3D laboratory experiment (Table 22.17) with previously measured D_{aT} values (COx, OPA and

- BC clays, Table 22.18) indicates that migration process in all studied clays is characterized by almost the same values of the apparent diffusion coefficient.
7. The obtained values of sorption parameters, R and K_d , for Sr-90 in the 3D experiment with CBlue clay are rather close to the relevant parameters characterizing the sorption of Sr-90 in diffusion experiments with compacted COx and OPA clay samples: the coefficient R (Table 22.17) is within the range of 14.9–22 measured in COx and OPA clays (Table 22.17), and $K_d \approx 2 \text{ cm}^3/\text{g}$, which is about twice as large as the average value from Table 22.19.
 8. The comparison of data from Table 22.17 and Table 22.12 shows that the diffusion of sorbed radionuclides in a compacted (undisturbed) material, characterized by the apparent diffusion coefficients, is much slower relatively to the diffusion of the same radionuclides in packing (disturbed/disintegrated) clay samples: the apparent diffusion coefficients for both Cl-36 and Sr-90 in the first set of experiments with clay pastes were significantly higher (up to an order of magnitude) than in the 3D experiment. From the latter it follows that modeling of radionuclide transport based on data from experiments with packing clays can overestimate migration process intensity, and the resulting forecasts can be too conservative.
 9. The batch sorption experiments with Vkt clay resulted in the distribution coefficients, K_d , which are about 20 times higher (the average value is about $45 \text{ cm}^3/\text{g}$, Table 22.9 and 22.10) than $K_d (\approx 2 \text{ cm}^3/\text{g})$ from diffusion experiments with compacted CBlue clay.

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Chapter 23

Tomsk-7 and Krasnoyarsk-26 Sites for Deep-Well Injection Radioactive Waste Disposal, and Lake Karachai Site of Near-Surface Disposal of Radioactive Brine

This experimental study was motivated by the need to carry out a safety assessment focused on the scientific understanding and measurement of the consequences of operations with radioactive waste (RW) at two chemical plants in Western Siberia. The industrial cycles of these plants are aimed at the production of nuclear weapon components and isotopes for medical and research needs. Both sites are associated with two systems of injection wells, which are used for disposal of low-level (LLW) and intermediate-level (ILW) radioactive wastes in deep geological formations. The solute transport properties of these formations are of special interest for long-term radionuclide migration forecasting.

Another set of experiments has been conducted to study sorption-like processes occurring in an aquifer affected by the leakage of radioactive brine from a surface reservoir, Lake Karachai (Sect. 15.1).

23.1 Nonideal Behavior of Sorption Curves Observed in Batch Tests with Core Material from the Tomsk-7 Site

The hydrogeological conditions in the site where the deep-well injection RW disposal site is situated has been given above (see Sect. 3.4.4). The recharge (injection flow rate) varies from 200 (for ILW) to 3,000 (for LLW) m^3d^{-1} , and the total activity of the waste varies from $3.7 \cdot 10^4$ to $3.7 \cdot 10^8 \text{ BqL}^{-1}$ (Rybalchenko et al. 1998, 2005; Zubkov et al. 2005). The radionuclide composition of the wastes is represented by the following fission products: Sr-90, Cs-137(-134), Ru-106, Zr-95, Nb-95, Ce-144 and some others. The actinides include Pu-239(-238,-240), Am-241 and Np-237.

The injection of ILW (Recharge well cluster 18 a, Sect. 3.4.4) into a deep geological formation at the site is accompanied by heat evolution. The temperature of the formation rises to more than 100°C . That is why the behavior of radionuclides in the subsurface environment is studied with batch laboratory experiments, which have been conducted under elevated temperature ($T = 70^\circ\text{C}$) and pressure ($P = 3 \text{ MPa}$) conditions. This pressure corresponds to an overburden of about 300 m.

These experimental results are compared with data previously obtained under room conditions ($T = 20^{\circ}\text{C}$ and $P = 0.1\text{ MPa}$).

During a natural attenuation period which is expected to start when the injection of the waste is stopped and the contaminants are supposed to be flushed out of pores by fresh water, the desorption process will play a dominating role in the transport of the waste. Thus, an experimental study of desorption is of special interest for determining the long-term impacts of the waste (Rumynin et al. 2002, 2005).

This work is not aimed to give a complete description of the entire complex of the very complicated physicochemical interactions accompanying the migration of radioactive solutions in the subsurface environment. These processes, in particular, lead to transformations of mineral rock phase, making it more difficult to predict radionuclide transport in the site of deep-well injection of liquid RW.

The purposes of this study are: (1) to identify the principal mechanisms responsible for sorption hysteresis under different geochemical, temperature and pressure conditions; (2) to develop analytical and numerical models which take into account (a) the microscopic heterogeneity of multi-mineral aquifers, and (b) variations of the external chemical potential resulting from the rate-limited transformations of the mineral phase; and (3) to demonstrate how the latter processes may affect the mobility of the radionuclides in the subsurface environment.

23.1.1 Materials, Methods, and Experimental Series

Several series of laboratory batch experiments with Sr-90 and Cs-137 were carried out for studying sorption–desorption processes. The experiments differ in (a) the radionuclide composition of the liquid phase, (b) the composition of solutions used at the sorption and desorption stages of the experiments, (c) the temperature/pressure regime of the experiments.

The liquid phase for the adsorption stage was represented by a synthesized groundwater (Table 23.1) or an acid ($\text{pH} = 3$) solution of NaNO_3 (10 gL^{-1}), which includes the following cations of trivalent and bivalent metals (gL^{-1}): Ni^{3+} (0.33), Cr^{3+} (0.86), Mn^{2+} (0.30).

The desorption of previously adsorbed radionuclides was performed using the same sodium nitrate solution, or the synthesized groundwater. The temperature in experiments was varied from 20 to 70°C . Pressure steps were varied between 0.1 and 3 MPa. Thus, a wide range of conditions was simulated in the laboratory, to cover different stages of the migration processes in groundwater.

Table 23.1 Groundwater chemistry (a major horizon for radioactive waste disposal)

Anions, mgL^{-1}					Cations, mgL^{-1}			pH
CO_3^{2-}	HCO_3^-	NO_3^-	SO_4^{2-}	Cl^-	Na^+	Ca^{2+}	Mg^{2+}	
1.49	234	0.6	2.47	6.43	111.2	3.7	0.6	7.6–8.0

Table 23.2 Sediment mineralogical composition

No.	Mineral	Lab data, % mass.	Type of reactive sites
1	Plagioclase	2.6	1
2	Biotite	7.6	2
3	Hydromica	11.7	2
4	Montmorillonite	11.4	2
5	Quartz	63	1
6	Carbonates	1.1	1
7	Rutile	0.3	1
8	Pyrolusite	0	1
9	Total mass of mineral phase, g	98.04	

Samples of unconsolidated sediment, represented by clayey sand, were taken from a potentially contaminated aquifer. A geosorbent (aquifer material) was a mixture of different lithological types of the sediment (an “average sample”). The artificially prepared mixture contains minerals (Table 23.2) with different adsorption properties, as well as minerals that potentially dissolve in acid solutions.

Each laboratory experiment used 1- or 2-g sand samples (previously conditioned using synthesized groundwater) of mass m_s . The volume of the solution (V) was 10 or 20 ml, so the liquid/solid ratio (L:S) was 10 in all experiments.

In the set-up of the laboratory tests, the kinetic stages of the adsorption and multi-step desorption of the radionuclides Cs-137 and Sr-90 were controlled reliably. The solutions were monitored by HPGe-MCA gamma counting system and beta scintillation counting of Sr/Y to determine Cs-137 and Sr-90 concentrations. Water samples were analyzed by atomic adsorption spectrometry for cations that might compete with radionuclides for adsorption sites. pH measurements were made with a combination electrode.

For the identification of the sorption and desorption isotherm (a type of graph in the coordinates N^s/N^d versus C , where N^s and N^d are the concentrations of the radionuclide in the solid phase at adsorption and desorption stages, respectively; C is the radionuclide's concentration in solution), several initial concentrations, C_i , of radionuclides were used; the test concentration range was $3.7 \cdot (10^5\text{--}10^8) \text{ BqL}^{-1}$. These concentrations were close to the concentrations detected in the radioactive waste. The concentration in the solid phase, $N^{s/d}$, was normalized to the volume of the tested sediment (the bulk density of dry aquifer sediment, ρ_b , was assumed to be 1.7 gcm^{-3}).

The composition of the solutions used for the sorption and desorption experiments and pressure and temperature conditions are summarized in Tables 23.3 and 23.4. The indices for the experimental series are explained in the notes for Table 23.3.

Table 23.3 Laboratory series (at $T = 20^{\circ}\text{C}$ and $P = P_{\text{atm}}$)^a

Radionuclide	Solution			
	Sorption		Desorption	
	Groundwater	NaNO ₃	Groundwater	NaNO ₃
Sr-90	Sr-GW	Sr-Na	Sr-Na-GW Sr-GW-GW	Sr-Na-Na
Cs-137	–	Cs-Na	Cs-Na-GW	Cs-Na-Na

^aGW and Na mean groundwater and sodium nitrate solution, respectively; Sr-GW is sorption of Sr-90 in groundwater solution; Sr(Cs)-Na is the sorption of Sr-90 (Cs-137) in sodium nitrate solution; Sr(Cs)-Na-Na is the sorption of Sr-90 (Cs-137) in sodium nitrate solution and desorption under the same conditions (in the same environment); Sr(Cs)-Na-GW is the sorption of Sr-90 (Cs-137) in sodium nitrate solution and desorption under the groundwater conditions; Sr-GW-GW is the sorption and desorption of Sr-90 in groundwater

Table 23.4 Laboratory series (experiments under elevated temperature/pressure conditions)^a

Radionuclide	Desorption	$T = 70^{\circ}\text{C}$, $P = P_{\text{atm}}$	$T = 70^{\circ}\text{C}$, $P = 3\text{ MPa}$
Sr-90	GW	Sr-Na-GW-70	Sr-Na-GW-70-3
Cs-137	NaNO ₃	Cs-Na-Na-70	Cs-Na-Na-70-3
	GW	Cs-Na-GW-70	Cs-Na-GW-70-3

^aRadionuclide sorption took place in sodium nitrate solution environment

23.1.2 Results: Qualitative Analysis

23.1.2.1 Variations in the Major Component Composition and pH of the Solution

Monitoring the concentration change of major components in liquid phase during the process of multi-step flushing of the sand samples by acid sodium nitrate solution indicates (Fig. 23.1a) that the first interaction between the sand and solution results in a sharp rise in the concentration of calcium (up to 100mgL^{-1}), magnesium (up to 50mgL^{-1}), strontium (up to 4.8mgL^{-1}), and potassium ions (up to 7.9mgL^{-1}). These concentrations significantly exceed (up to one to two orders of magnitude) the background concentrations of the components in the formation water (Table 23.1) as well as in the flushing solution. Apparently, active dissolution of carbonate minerals and displacement of cations from exchange complex occur at this stage.

The subsequent iterations (incubation periods) show a decrease in the concentrations of the cations in solution. Thus, the multi-step interactions between the solid and liquid phases lead to a depletion in dissolving salt reserves (minerals) and to a redistribution of the exchanging cations in the system. Also, the process may be accompanied by an alteration of silica (first of all mica) minerals. The “acid–alkaline” reaction of the solution changes slightly (pH from 3.05 to 3.20).

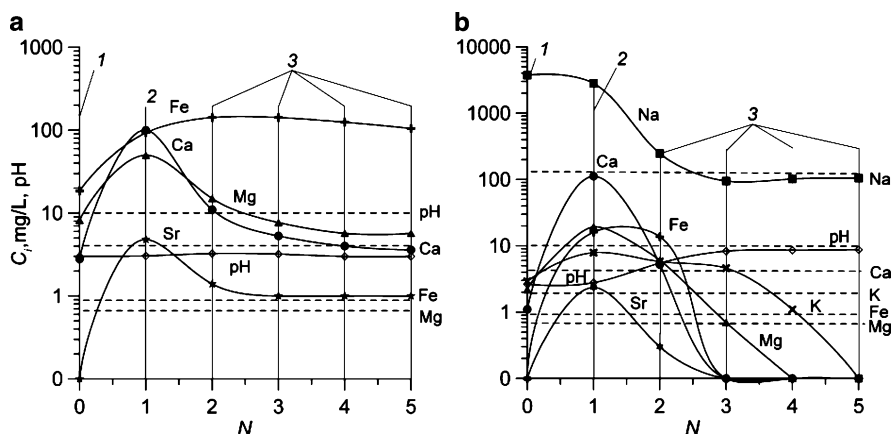


Fig. 23.1 A change in the major component composition of solution, which was measured in the multi-step flashing of the sediment by (a) solution of NaNO_3 and (b) groundwater; dotted lines show the initial composition of groundwater; (1) displacing solution (NaNO_3 , before the sorption step), (2) equilibrium at the sorption step, (3) equilibrium at the desorption steps; N is the number of the flushing step (at the first sorption step, the sample was in contact with the NaNO_3 solution)

The system's response to the substitution of the acid solution at the first and subsequent desorption steps for the synthesized ("fresh") groundwater (Fig. 23.1b) is as follows: a rather quick (two desorption steps) removal from the system occurs for practically all of the major cations (Ca^{2+} , Mg^{2+} , Fe^{3+}) as well as stable strontium (Sr^{2+}). The potassium-ion concentration (K^+) decreases more slowly. Of the cations that were present in the solution before flushing of the aquifer sediment by the synthesized water, only sodium ions remain in the system at concentrations near background level. During desorption, solution pH increases dramatically from 2.8 to 8.7.

Overall, the presented data suggest that the hydrochemical conditions in the system radically change in the course of experiments. They demonstrate a variable composition of principal cations, varying from one step to another, which in this context can be considered as potential-controlling. Moreover, this composition differs from the equilibrium one we had during adsorption. Therefore, obviously, the adsorption and desorption of radionuclides take place under nonequivalent conditions; moreover, radionuclide desorption proceeds under different thermodynamic conditions.

23.1.2.2 Kinetics of the Process: Experiments Under Room Conditions

Analysis of the kinetic curves (Fig. 23.2a, b), obtained under standard reference (or room) conditions, $P = P_{\text{atm}} = 0.1 \text{ MPa}$, $T = 20^\circ\text{C}$, shows that, in general, sorption-desorption can be considered as a transient (or non-equilibrium) process. However, the process tends to reach equilibrium in 7–10 days after the beginning of the experiment. No anomalous effects are observed. A period of one to two weeks is probably sufficient to reach a near-equilibrium state for the given experimental conditions.

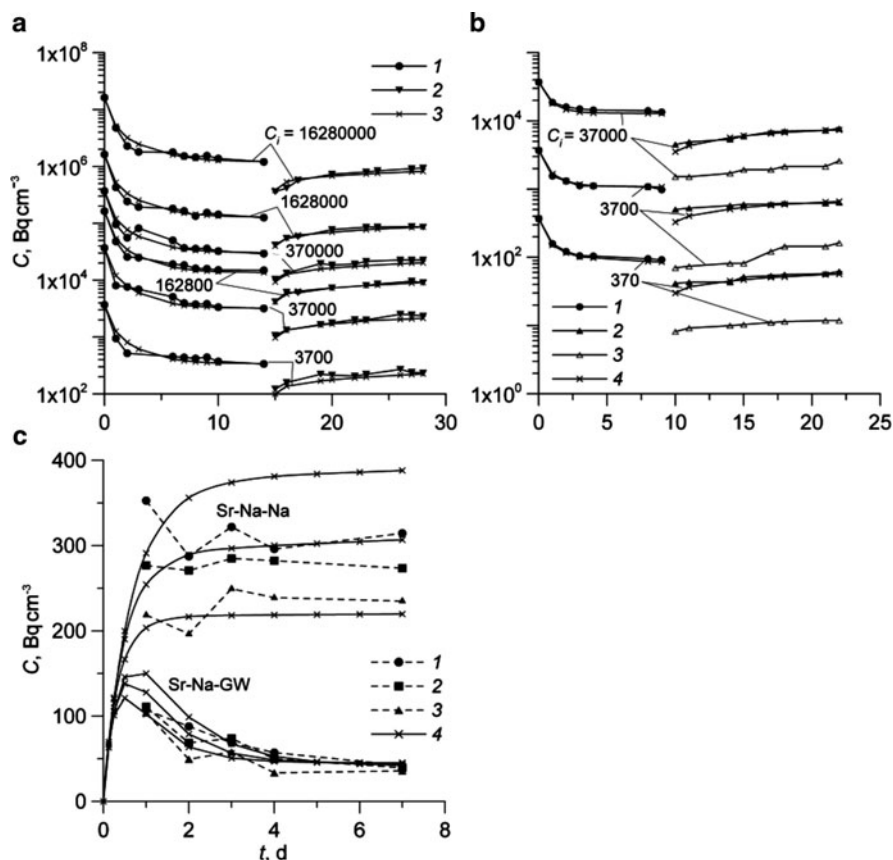


Fig. 23.2 Kinetic (experimental and predicted) curves of sorption and desorption (first step) periods. (a) Series Sr-GW-GW: (1) sorption – experimental data, (2) desorption – experimental data, (3) fitted curves. (b) Series Cs-Na-Na and Cs-Na-GW: (1) sorption in NaNO₃ environment, (2) desorption in NaNO₃ environment, (3) sorption in GW environment, (4) modeling curves for Cs-Na-Na series). (c) Desorption of Sr-90, series Sr-Na-Na and Sr-Na-GW: (1) $C_i = 3,700$ Bq cm⁻³, (2) $C_i = 37,000$ (scale 1/10) Bq cm⁻³, (3) $C_i = 370,000$ (scale 1/100) Bq cm⁻³, (4) modeling curves; C_i (Bq cm⁻³) is radionuclide concentration in solution at the sorption step

Kinetic desorption curves in the experimental series Sr-Na-GW display an anomalous nature (Fig. 23.2c). This was the case when Sr-90, which was adsorbed from the sodium nitrate solution, was washed out by fresh water. The desorption of a radionuclide, which is dominating at the beginning of the interaction between the contaminated porous material and water, becomes negligible in comparison with the adsorption dominating at the latest periods. This is in contrast to the expected increase of the radionuclide concentration in solution.

The fitting of the curves to data points in Fig. 23.2 is discussed in Sect. 23.1.3.

23.1.2.3 Kinetics of the Process: Experiments Under Elevated Temperature and Pressure

The first set of experimental series with radionuclides (Sr-Na-GW-70, Cs-Na-Na-70 and Cs-Na-GW-70) (Table 23.4) was carried out at the temperature of 70°C and under normal atmospheric pressure ($P = P_{\text{atm}}$). Another set of experiments (Sr-Na-GW-70-3, Cs-Na-Na-70-3 and Cs-Na-GW-70-3) was carried out at the same temperature, but at a pressure of 3 MPa.

$$T = 70^{\circ}\text{C} \text{ and } P = P_{\text{atm}}$$

At the sorption step of the experimental series with **Sr-90**, the concentration function, C , was found to change slowly (Fig. 23.3a–c). This suggests that the process is affected by the dissolution of carbonate minerals and/or the hydrolysis of alumina silicates. The extremes that were noted in the desorption kinetic curves under room conditions were not observed in this case.

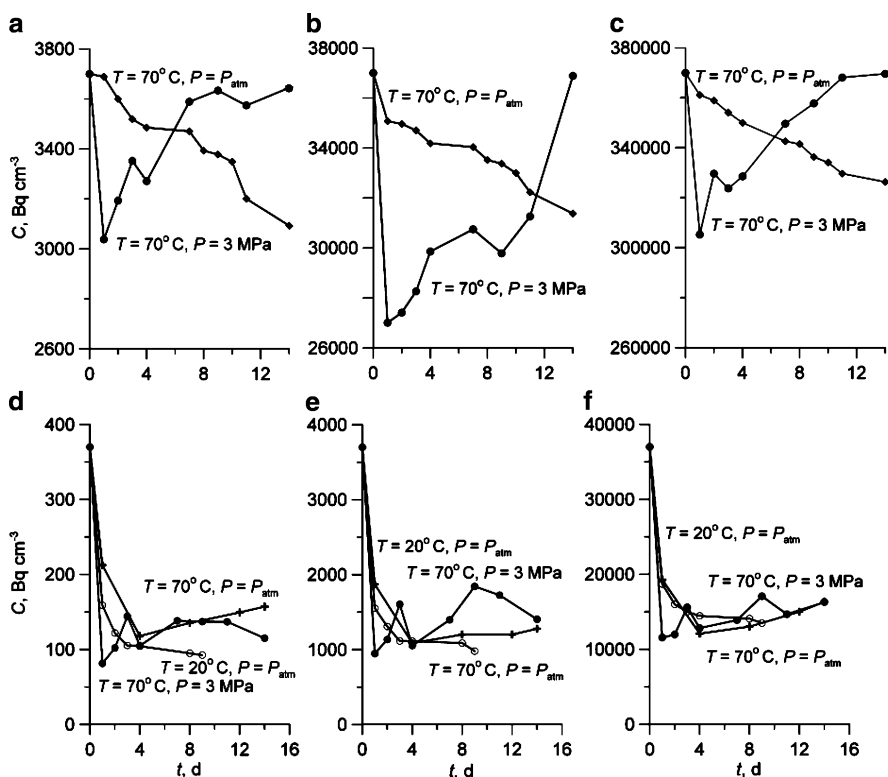


Fig. 23.3 The influence of the temperature (T) and pressure (P) on sorption kinetics. (a, b, c) Sr-90 sorption: (a) $C_i = 3,700 \text{ Bq cm}^{-3}$, (b) $C_i = 37,000 \text{ Bq cm}^{-3}$, (c) $C_i = 370,000 \text{ Bq cm}^{-3}$. (d, e, f) Cs-137 sorption: (d) $C_i = 370 \text{ Bq cm}^{-3}$, (e) $C_i = 3,700 \text{ Bq cm}^{-3}$, (f) $C_i = 37,000 \text{ Bq cm}^{-3}$.

Sorption curves obtained for **Cs-137** with hot and cold acid solutions (Fig. 23.3d–f) did not differ much from each other. One may anticipate that the mineral dissolution produces ions that did not compete for the adsorption sites with Cs-137.

$$T = 70^{\circ}\text{C} \text{ and } P = 3 \text{ MPa}$$

Breakthrough curves obtained at the sorption stage of the experiments with NaNO_3 solution have shown a non-monotonic character (Fig. 23.3). During the first days from the beginning of experiments, a drop was observed in radionuclide concentration in NaNO_3 solution. Later, however, an increase in the radionuclide content in the solution was noted. This effect is most pronounced for **Sr-90**: its concentration at the end of the sorption experiment (14 days) reaches the initial values (Fig. 23.3a–c). This means that Sr-90 was adsorbed at first by the clayey sand in large quantities. Then it was completely desorbed into the solution, so that the sediment contained no contaminants. The calculated apparent constant of the sorption distribution is supposed to be zero (i.e. the release of Sr-90 is about 100%). The release of **Cs-137** reaches 15–20%.

The phenomenon established experimentally can be explained if we take into account that sorption equilibrium is controlled by dissolution kinetics of minerals in the solid phase. Indeed, sorption and desorption are sufficiently rapid processes compared with mineral dissolution. Therefore, Sr-90 is actively adsorbed at first, when the solution is undersaturated by competing bivalent cations (principally, calcium). Later, however, the concentration of these cations gradually increases, due to dissolution of carbonate minerals. This leads to the release of Sr-90 from the exchange complex of rock. The degree of solution saturation by calcium ions is proportional to the concentration (partial pressure) of carbon dioxide, whose solubility rises with pressure increase. Therefore, at the elevated pressure, calcium concentration can reach values that indicate that practically all Sr-90 has been released to the solution.

At elevated temperature and pressure, the acid solution of NaNO_3 can also dissolve some silicate minerals, for example hydro-mica. In this case, the solution must be enriched gradually with potassium ions that compete with Cs-137 for the exchange positions on the matrix. Therefore, it can be supposed that the accumulation of potassium ions in the solution leads to the release of previously adsorbed Cs-137 (series Cs-Na- Na/GW-70-3, Fig. 23.3d–f).

Thus, we have received an experimental evidence of a fact that is of importance for subsequent migration studies: an increase in temperature and pressure in the system, at which transformation of mineral rock phase takes place, leads to its saturation with components, whose concentrations are large enough to suppress the adsorption process. Thus, under such conditions, occurring near injection wells at the RW disposal site, Sr-90 behaves as a *chemically inert component*.

23.1.2.4 Equilibrium Relationships and Isotherms

The best fit of the log-transformed experimental data (Figs. 23.4–23.6) characterizing sorption equilibrium is a straight line. This means that sorption isotherms are of the Freundlich type (Sect. 19.1):

$$N = K_F C^n, \text{ or } \ln N = \ln K_F + n \ln C, \quad (23.1)$$

where C is the equilibrium concentration in the solution; N is the concentration on the solid phase at the sorption stage of the experiment; K_F and n are the linear and exponential Freundlich constants, respectively.

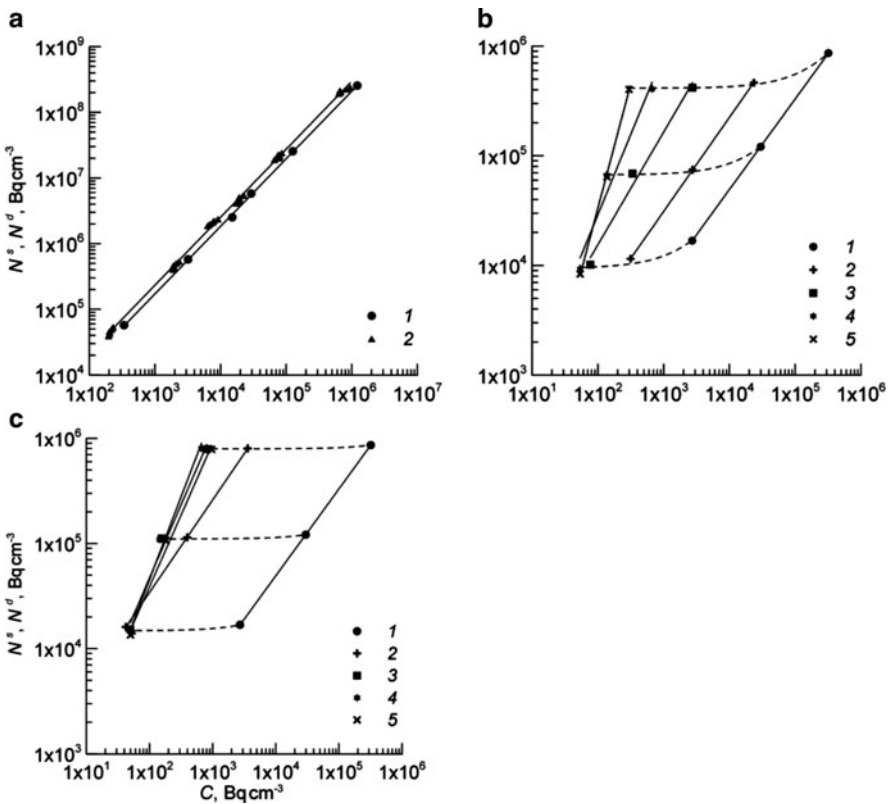
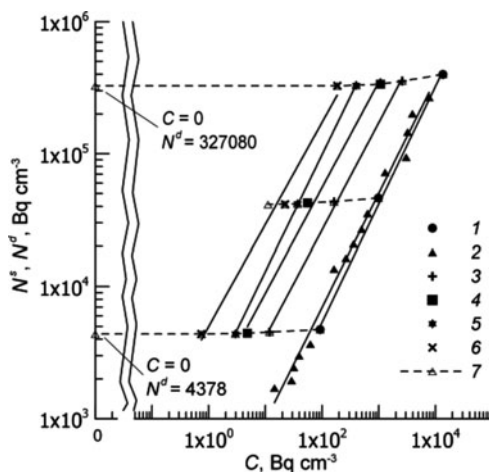


Fig. 23.4 Isotherms of sorption and desorption of Sr-90 (double-log scale) for experimental series. (a) Sr-GW-GW: (1) sorption, fitting curve ($N^s = 140.7C^{1.03}$), (2) desorption, fitting curve ($N^d = 183.5C^{1.04}$). (b) Sr-Na-Na: (1) sorption ($N^s = 24.6C^{0.83}$), (2) desorption, step 1 ($N^d = 83.4C^{0.86}$), (3) desorption, step 2 ($N^d = 136.9C^{1.03}$), (4) desorption, step 3 ($N^d = 34.4C^{1.57}$), (5) desorption, step 4 ($N^d = 1.0C^{2.26}$). (c) Sr-Na-GW: (1) sorption ($N^s = 24.6C^{0.83}$), (2) desorption, step 1 ($N^d = 598.2C^{0.88}$), (3) desorption, step 2 ($N^d = 77.0C^{1.39}$), (4) desorption, step 3 ($N^d = 33.0C^{1.57}$), (5) desorption, step 4 ($N^d = 72.6C^{1.36}$).

Fig. 23.5 Double-log scale isotherms of Cs-137 sorption-desorption (experimental series Cs-Na-Na and Cs-Na-GW): (1) sorption in NaNO_3 solution ($N^s = 90.0C^{0.89}$); (2) desorption in NaNO_3 ($N^d = 133.0C^{0.86}$); (3) desorption in SGW: 1 step ($N^d = 642.3C^{0.81}$), (4) 2 step ($N^d = 1417.9C^{0.80}$), (5) 3 step ($N^d = 1706.0C^{0.88}$), (6) 4 step ($N^d = 4982.2C^{0.77}$), (7) 5 step



Analysis of the experimental results shows that, with a few exceptions, all desorption concentration points are located above the sorption isotherms, i.e. desorption isotherms do not coincide with sorption isotherms (Figs. 23.4–23.6). The experimental data display a hysteresis in the adsorption process. Probably, a new chemical equilibrium is reached at each of the desorption steps. In this case the line connecting the measured points $C - N$ can be considered as a desorption isotherm. Analysis of the experimental results indicates that the desorption process can be described by the Freundlich relationship (23.1) as well. Then $N \equiv N^d$ is the concentration in the solid phase at the desorption stage, $K_F \equiv K_F^d$ and $n \equiv n^d$ are the linear and exponential desorption constants, respectively, and d is desorption (backward reaction). At the same time, there are some deviations of the experimental measurements from Eq. 23.1 caused by the irreversibility of sorption.

It should be mentioned that the low-concentration domains of desorption isotherms are characterized insufficiently, since each subsequent desorption step gradually shifted the experimental process into the domain lying at the accuracy limit of analytically measured concentrations; this is a cause of the difficulties in studying the “irreversible” component of sorption.

23.1.2.5 Experiments Under Room Conditions

Strontium-90

In the system with synthetic groundwater (Sr-GW-GW), the sorption and desorption isotherms do not differ much (Fig. 23.4a, Table 23.5). A minor divergence of the two stages of the experiments can be explained by process kinetics. The presence of the dissolved sodium nitrate and products of its interaction with the mineral phase in solution decreases the sorption capacity of the sediment, resulting in a nonlinear process (n is less than one) (Fig. 23.4b, Table 23.5).

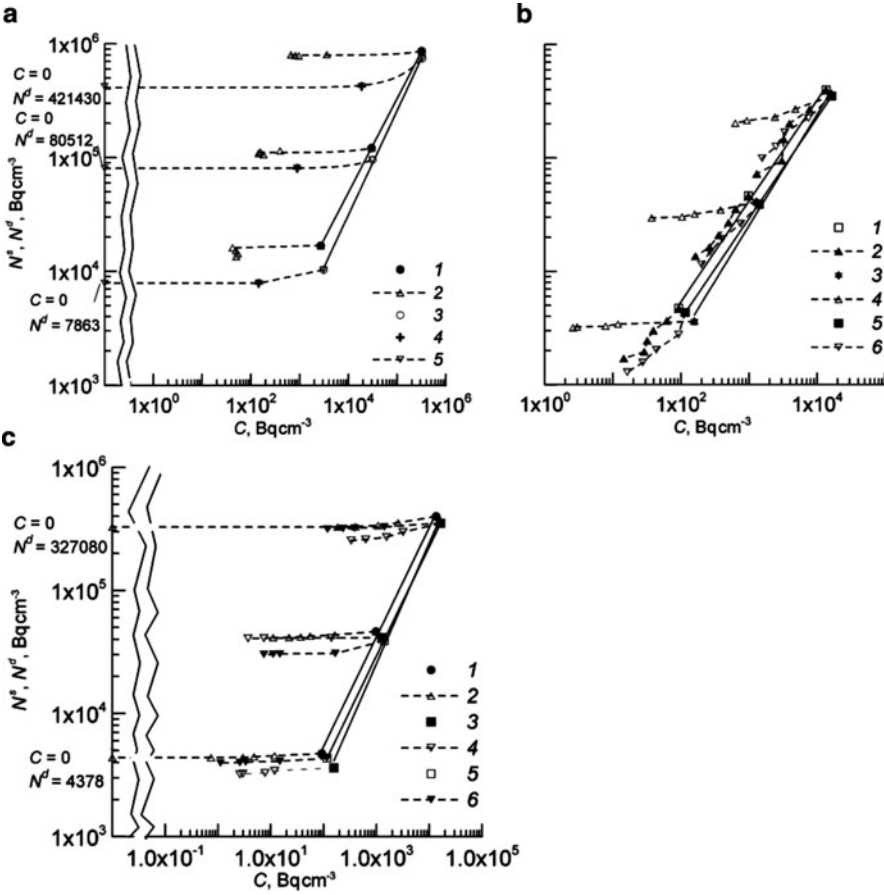


Fig. 23.6 The influence of the temperature and pressure on sorption and desorption isotherms. (a–c) Experimental series. (a) Sr-Na-GW: (1) sorption ($T = 20^\circ\text{C}$, $P = P_{\text{atm}}$); (2) desorption ($T = 20^\circ\text{C}$, $P = P_{\text{atm}}$); (3) sorption ($T = 70^\circ\text{C}$, $P = P_{\text{atm}}$); (4) desorption ($T = 70^\circ\text{C}$, $P = P_{\text{atm}}$, step 1); (5) desorption ($T = 70^\circ\text{C}$, $P = P_{\text{atm}}$, 2, 3, 4 steps). (b) Cs-Na-Na: (1) sorption ($T = 20^\circ\text{C}$, $P = P_{\text{atm}}$); (2) desorption ($T = 20^\circ\text{C}$, $P = P_{\text{atm}}$); (3) sorption ($T = 70^\circ\text{C}$, $P = P_{\text{atm}}$); (4) desorption ($T = 70^\circ\text{C}$, $P = P_{\text{atm}}$); (5) sorption ($T = 70^\circ\text{C}$, $P = 3 \text{ MPa}$); (6) desorption ($T = 70^\circ\text{C}$, $P = 3 \text{ MPa}$). (c) Cs-Na-GW: (1) sorption ($T = 20^\circ\text{C}$, $P = P_{\text{atm}}$); (2) desorption ($T = 20^\circ\text{C}$, $P = P_{\text{atm}}$); (3) sorption ($T = 70^\circ\text{C}$, $P = P_{\text{atm}}$); (4) desorption ($T = 70^\circ\text{C}$, $P = P_{\text{atm}}$); (5) sorption ($T = 70^\circ\text{C}$, $P = 3 \text{ MPa}$); (6) desorption ($T = 70^\circ\text{C}$, $P = 3 \text{ MPa}$)

The observed sorption–desorption hysteresis (Fig. 23.4b, c) can result from variations of the major cations’ content and pH. Thus, the chemical equilibrium at the first desorption step shows the presence of a noticeably smaller amount of the displaced cations in the solution, compared with the adsorption stage. Therefore, the equilibrium conditions differ from the conditions at the adsorption stage. The same tendency is also seen in the subsequent desorption steps, which are characterized by a gradual release of cations of alkali-earth metals from the system. Although the

Table 23.5 Freundlich sorption–desorption constants from the batch experiments

		Sr-90						Cs-137			
Stage of experiment		Sr-GW-GW		Sr-Na-Na		Sr-Na-GW		Cs-Na-Na		Cs-Na-GW	
		K_F^a	n	K_F	n	K_F	n	K_F	n	K_F	n
Sorption		141	1.03	24.6	0.83	24.6	0.83	90.6	0.89	90.6	0.89
Desorption (step number)	1			83.4	0.86	598	0.88			642	0.81
	2			137	1.03	77.0	1.39			1418	0.80
	3	183.5	1.04	34.4	1.46	33.0	1.57	133	0.86	1706	0.88
	4			1.0	2.26	72.6	1.36			4982	0.77
	5			ND ^b	ND	ND	ND			IRA ^c	IRA

^aUnit [(cm³/Bq)ⁿ⁻¹]^bNo data available^cIrreversible sorption

desorption equilibrium is described by the same type of isotherm (Fig. 23.4b), the values of K_F and n in Eq. 23.1 change from one step to another (Table 23.5).

When desorption takes place into synthetic groundwater (series Sr-Na-GW), Sr-90 releases less readily from the reactive (adsorption) sites compared with desorption into the acid solution of NaNO₃. Therefore, the residual concentration of Sr-90 on the mineral phase (N^d) is higher than in Sr-Na-Na series (Fig. 23.4c). The first desorption isotherm is characterized by a coefficient n ($\equiv n^d$), which is close to its sorption coefficient n ; the value for K_F ($\equiv K_F^d$) rises because the solution is of a much lower ionic strength than it was before the desorption step (Table 23.5). As in the preceding case, further desorption steps lead to an increase in the constant n and a drop in the values of the coefficient K_F .

Cesium-137

The sorption ability of Cs-137 is higher than that of Sr-90: K_F (series Cs-Na) $\gg K_F$ (series Sr-Na), Table 23.5. However, a decrease in the saturation of the solution by cations of alkali-earth metals at the desorption steps in the experimental series Cs-Na-Na in Fig. 23.5, does not lead to a retention of Cs-137 in the solid phase. Very likely, the equilibrium in the system is controlled exclusively by the ionic strength of solution, which changes slightly from one desorption step to the next.

A step-by-step wash-out of the contaminated sediment with the synthesized groundwater (series Cs-Na-GW) leads to a displacement of the desorption isotherms along the concentration axis, C , with respect to the sorption line (Fig. 23.5). In contrast to the previous experiments, however, the desorption isotherms remain approximately parallel to the sorption isotherm up to the fourth desorption step: the linear coefficient K_F ($\equiv K_F^d$) increases considerably, while the exponential index n ($\equiv n^d$) changes only slightly (Table 23.5). Flushing the sand samples, which were contaminated at the adsorption stage, with fresh water did not result in a release of a detectable amount of Cs-137 from the mineral phase after five washes (Fig. 23.5).

23.1.2.6 Experiments Under Elevated Temperature and Pressure

$$T = 70^{\circ}\text{C} \text{ and } P = P_{\text{atm}}$$

Experimental data and models characterizing the equilibrium of the system are presented in Fig. 23.6 and Table 23.6. A rise of the solution temperature resulted in an apparent decrease of the capacity of the porous medium to adsorb radionuclides. Furthermore, an increase in the temperature of the system resulted in more linear sorption. This behavior is explained in Sect. 23.1.2.3. An increase in the temperature leads to a more intensive dissolution of carbonate and silicate minerals. Therefore, the solution at higher temperature is characterized by greater concentrations of the bivalent cations of alkaline earth metals than at $T = 20^{\circ}\text{C}$. These ions compete with the Sr-90 for adsorption sites, thereby causing faster dissolution at $T = 70^{\circ}\text{C}$.

Further analysis of the batch experiment with **Sr-90** (Sr-Na-GW-70) demonstrates that a rise in the temperature made the sorption process irreversible (Fig. 23.6a). Starting with the second desorption step, the solution loses radioactivity completely ($C = 0$). The radionuclide could not be removed from the exchanged complex of the rock due to a strong deficiency of bivalent cations in the solution, which resulted from the first interaction of the rock with the hot acid solution. In contrast to the series Cs-Na-Na ($T = 20^{\circ}\text{C}$), no irreversibility of the **Cs-137** sorption was noted in the experimental series Cs-Na-GW-70 (Fig. 23.6b).

$$T = 70^{\circ}\text{C} \text{ and } P = 3 \text{ MPa}$$

The measured amount of **Sr-90** in the solid phase at the end of the adsorption experiments is close to zero. The results of the sorption experiments with **Cs-137** under the same conditions were close to the experiments with hot solution conducted under atmospheric pressure. The relevant sorption isotherms in Fig. 23.6b and Fig. 23.6c practically coincide. As seen in Fig. 23.6b, the desorption points deviated less from the sorption isotherm (desorption into the NaNO_3 solution, series Cs-Na-Na-70-3)

Table 23.6 Fitting equilibrium sorption constants

Radio nuclide	$T = 20^{\circ}\text{C}, P = P_{\text{atm}}$		$T = 70^{\circ}\text{C}, P = P_{\text{atm}}$		$T = 70^{\circ}\text{C}, P = 3 \text{ MPa}$	
	K_F^a	n	K_F	n	K_F	n
Sr-90 (Sr-GW)	140	1.03	ND ^b	ND	ND	ND
Sr-90 (Sr-Na)	24.6	0.83	6.7	0.92	NS ^c	NS
Cs-137 (Cs-Na)	90.0	0.89	29.1	0.98	63.8	0.89

^aUnit see in Table 23.5

^bNo data available

^cNo sorption

than what was observed in the experiment at $T = 70^\circ\text{C}$ and $P = P_{\text{atm}}$ (series Cs-Na-Na-70). The desorbed amount of Cs-137 in series Cs-Na-GW-70-3 is almost the same as in the previous series Cs-Na-GW-70 (Fig. 23.6c).

23.1.3 Modeling Results and Discussion

An application of the model of heterogeneous sorption sites to experiments with **Sr-90** is limited to the experimental series Sr-GW-GW because the hydrogeochemical environment remained nearly constant. In the remaining experiments, the kinetics of sorption–desorption is overshadowed by dissolution processes of some constituents of the mineral phase that affects the sorption kinetics and equilibrium. Experiments with **Cs-137** are less sensitive to the concentration of major cations in solution than those with Sr-90, since Cs-137 prefers to adsorb on the solid phase in a no-exchange manner (Klechkovsky and Gulyakin 1958; EPA 1999).

23.1.3.1 Application of the Kinetic Model of Dual-Site Adsorption

In the modeling discussed below, the value of the fraction, f , was assumed to be 0.75 because we supposed that approximately 75% of the clayey sand consists of minerals with relatively weak mass-exchange (sorption) properties (quartz, feldspar, and carbonates; see Table 23.2). About 25% would consist of the “active” mineral geosorbents (clay and micaceous minerals, Table 23.2). We also assumed that $n_i^d = n_i^s \equiv n$ and $K_{Fi}^d = K_{Fi}^s \equiv K_{Fi}$ (with the exception of the series Sr-Na-GW).

Strontium-90

The experimental points, $C(t)$, in Fig. 23.2a of the sorption–desorption kinetics (*experimental series* Sr-GW-GW) agree well with the predicted curves calculated using the parameters represented in Table 23.7. The use of the parameters obtained during the simulation of the step-by-step desorption are also in good agreement with the experimental and modeling points (Fig. 23.7a). The values of the predicted concentration, C , were, however, smaller than the experimental data for lower concentrations. This may be related to the nonlinearity of the process, which was not taken into account during the mathematical formalization of the problem.

Analysis of the values of the fitting constants (Table 23.7) yields the following: (1) the distribution coefficient for the clay fraction, K_{F_2} , exceeds the values for the fraction of quartz, plagioclase, and carbonates, K_{F_1} , by a factor of about 50; (2) the kinetic desorption constants are noticeably smaller than the kinetic sorption constants; and (3) $\alpha_2^d < \alpha_1^d$.

The redistribution of the radionuclides between the reactive sorption sites at the desorption step (*experimental series* Sr-Na-GW) results in the *non-monotonic*

Table 23.7 Fitting parameters of the sorption–desorption experiments ($T = 20^{\circ}\text{C}$, $P = P_{\text{atm}}$)

n^c	$K_{F_1}^a$	$K_{F_2}^b$	$fK_{F_1} + (1-f)K_{F_2}$	$\alpha_1^{s,d}$	α_2^s	$\alpha_1^{d,f}$	$\alpha_2^{d,g}$
Sr-90: sorption–desorption in synthetic groundwater (Sr-GW-GW)							
1.03	10	532	141	60	60	10	5
Sr-90: desorption by synthetic groundwater (Sr-Na-GW)							
0.83	15	3000 ^h	761	100	100	15	3
Cs-137: sorption–desorption in NaNO ₃ solution (Cs-Na-Na)							
0.89	20	300	90	70	50	15	7

^{a–b}Linear sorption constants for sites of type 1 (a) and 2 (b), (Bq/cm^3)^{1–n}

^cExponential dimensionless constant

^{d–g}Kinetic sorption–desorption constants, d^{–1}

^h $K_{F_2}^d$ value

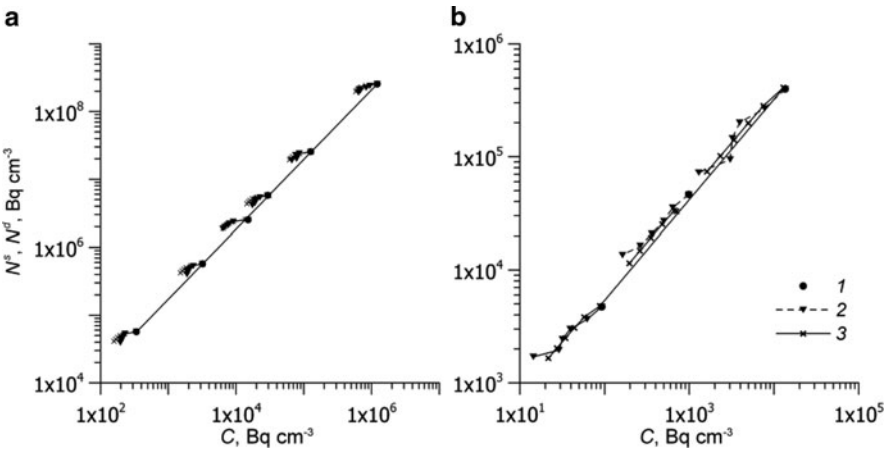
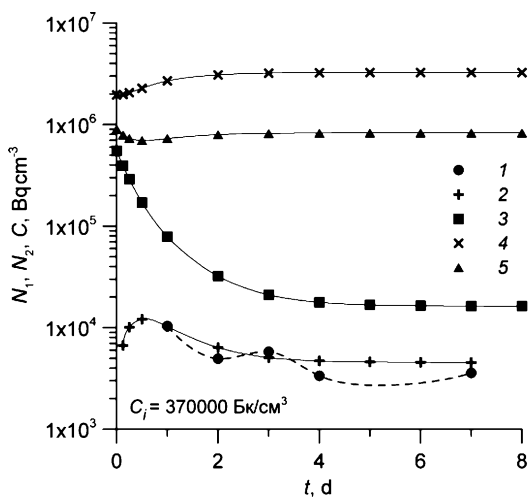


Fig. 23.7 Interpretation of the experimental sorption–desorption isotherms. (a) Series Sr-GW-GW; (b) series Cs-Na-Na. (1) Adsorption – experimental data, (2) desorption – experimental data, (3) modeling results

behavior of the concentration function, $C(t)$ (Fig. 23.2c). This can be modeled by increasing the value of the partial coefficient, K_{F_2} , which is responsible for the Sr-90 sorption by the sites of type 2 at the beginning of the interaction of the contaminated soil with initially radionuclide free groundwater. In this case, the radionuclides being released from sites of type 1 (characterizing relatively low values of K_{F_1} and increased values of α_1^d) then start to be kinetically adsorbed by the sites of type 2 with sharply increased values of the coefficient $K_{F_2} \gg K_{F_1}$ (Table 23.7). The overall effect of this model is shown by the line in Fig 23.2c. Figure 23.8 presents additional model data showing differently directed variation trends in concentrations N_1 and N_2 (Sect. 19.1.3.2). As can be seen, the nonmonotonic behavior of the total function N leads to the formation of a peak in the plot of $C(t)$.

Fig. 23.8 Dynamics of variations in major concentration functions. (1) Experimental data (Sr-90 concentration in liquid phase); (2, 3, 4, 5) modeling results: (2) C (concentration in liquid phase), (3) and (4) correspond to N_1 and N_2 , the concentrations in the composition of the solid phase (on the first and second type sites, respectively), (5) total concentration, $fN_1 + (1-f)N_2$



Cesium-137

The sorption–desorption stages of the experiment (*experimental series Cs-Na-Na*) have been modeled using a dual-site adsorption model, which is in excellent agreement with experimental data (dotted lines) (Figs. 23.2b and 23.7b). The values of fitting parameters for this model are given in Table 23.7; in particular, the values of the kinetic constants, α_i^s , are close to the corresponding values obtained for Sr-90. Moreover, the same relationship as that for Sr-90 ($\alpha_i^d < \alpha_i^s$) was observed in these experiments.

23.1.3.2 Application of the One-Site Kinetic Model of Adsorption with Concomitant Dissolution of Carbonate Minerals

This model gives an alternative conceptual basis for the interpretation of the hysteresis effects observed in laboratory tests carried out under elevated temperature and pressure.

Strontium-90

The experimental sorption curves of Sr-90 at the elevated temperature and pressure (*experimental series Sr-Na-70-3*, Fig. 23.3a–c) exhibited a well-expressed extreme character. They are satisfactorily described by Eq. 19.38 using a fitting parameter (Fig. 23.9a). Experimental and modeling results agree when sufficiently low values of the dissolution kinetic constant are applied (e.g., $\bar{\alpha} = 0.01 - 0.02$, $\alpha_2 = 0.15 - 0.30 \text{ d}^{-1}$).

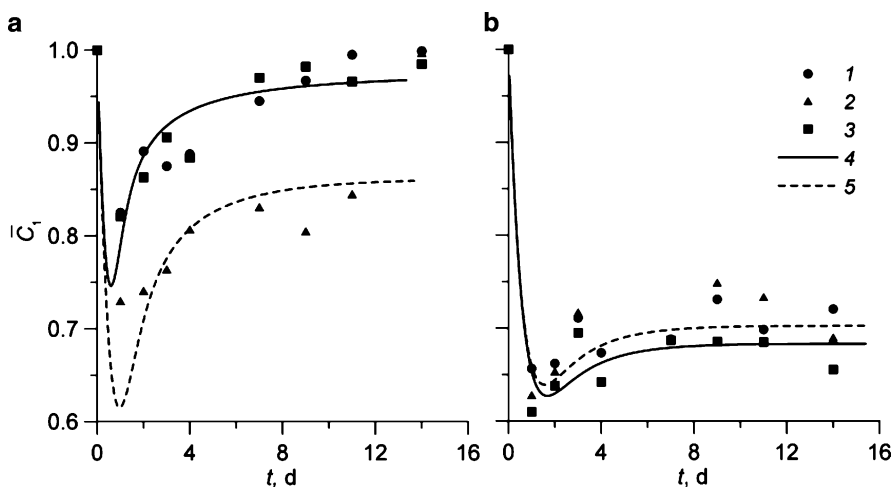


Fig. 23.9 Fitting curves for the sorption kinetics. (a) Sr-90. (1)–(3) are experimental data: (1) $C_i = 370,000 \text{ Bqcm}^{-3}$, (2) $C_i = 37,000 \text{ Bqcm}^{-3}$, (3) $C_i = 3,700 \text{ Bqcm}^{-3}$; (4)–(5) are modeling curves: (4) $\bar{C}_2^0 = 0.02$, $\alpha_2/\alpha_1 = 0.01$, (5) $\bar{C}_2^0 = 0.004$, $\alpha_2/\alpha_1 = 0.02$; other values: $a = 17$, $\bar{C}_2^{\text{sat}} = 90$, $\alpha_1 = 15 \text{ d}^{-1}$; (b) Cs-137. (1)–(3) are experimental data: (1) $C_i = 37,000 \text{ Bqcm}^{-3}$, (2) $C_i = 3,700 \text{ Bqcm}^{-3}$, (3) $C_i = 370 \text{ Bqcm}^{-3}$; (4)–(5) are modeling curves: (4) $\bar{C}_2^0 = 0.0017$, $\alpha_2/\alpha_1 = 0.02$, (5) $\bar{C}_2^0 = 0.002$, $\alpha_2/\alpha_1 = 0.02$; other values: $a = 17$, $\bar{C}_2^{\text{sat}} = 20$, $\alpha_1 = 25 \text{ d}^{-1}$

Cesium-137

Experimental data on sorption kinetics of Cs-137 (series Cs-Na-70-3, Fig. 23.3d–f) do not contradict the conceptual model as shown in Fig. 23.9b where the values of the fitting parameters were obtained by the substitution into Eq. 19.38. These parameters were also used for the calculation of isotherms presented in Fig. 23.10. In this procedure, the magnitude of the dimensionless concentration, $\bar{C}_2^{\text{sat}} = \bar{C}_2^{\text{sat}}(i)$ (where i is the number of the desorption step) was gradually decreased from one step to the next. The experimental and modeling values of C_1 and N_1 (for the specified values of a , $\bar{C}_2^0$, $\bar{\alpha}$, and $\Delta\bar{t}$) agreed with the appropriate variations in the concentration, $\bar{C}_2^{\text{sat}}$. The observed differences in the experimental and modeling results can be explained by a more complex nature of the relationship $N(C)$ in Eq. 19.18.

Overall, the calculations demonstrated the validity of the assumptions made above. Importantly, the calculations prove that rock mineral phase transformation has its effect on the rate and direction of sorption–desorption processes.

Experimental results are important for the analysis of radionuclide migration in groundwater. Thus, the set-up of the experiments can be associated with the simulation (“static/zero-dimensional” modeling) of the groundwater system’s response to an inflow of acid brine into the aquifer. The behavior of the principal solution components in the experiments with unconditioned sediment samples is similar to what is often observed at actual contaminated sites when the advancing front of the

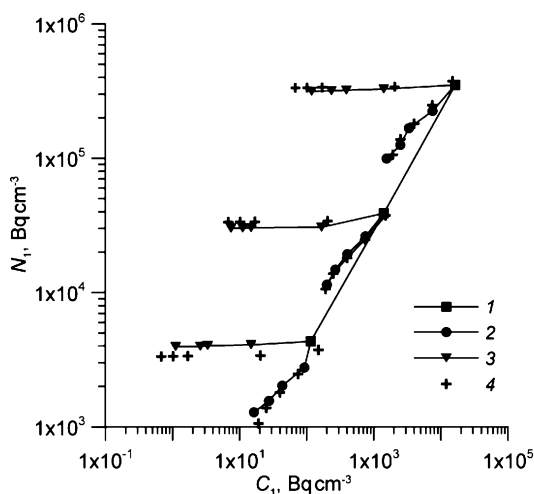


Fig. 23.10 Sorption and desorption of Cs-137 (series Cs-Na-Na and Cs-Na-GW): experimental and modeling data. (1) Sorption; (2) desorption: series Cs-Na-Na; (3) desorption: series Cs-Na-GW; (4) fitting points Eq. 19.38 Cs-Na-Na: $\bar{C}_2^{\text{sat}}(1) = 20$, $\bar{C}_2^{\text{sat}}(2) = 15$, $\bar{C}_2^{\text{sat}}(3) = 11$, $\bar{C}_2^{\text{sat}}(4) = 9$, $\bar{C}_2^{\text{sat}}(5) = 9$; Cs-Na-GW: $\bar{C}_2^{\text{sat}}(1) = 20$, $\bar{C}_2^{\text{sat}}(2) = 3$, $\bar{C}_2^{\text{sat}}(3) = 0.25$, $\bar{C}_2^{\text{sat}}(4) = 0.15$, $\bar{C}_2^{\text{sat}}(5) = 0.1$. Other parameters: $\bar{C}_2^0 = 0.002$, $\bar{\alpha} = 0.02$, $\alpha_1 = 25 \text{ d}^{-1}$, $\Delta t = 14 \text{ d}$, $a = 17$

inflowing solution displaces groundwater. In particular, such behavior was monitored at the Lake Karachai radioactive waste disposal site (Sect. 15.2) as well as at a number of sites in the Western Urals, Russian Federation, where subsurface reservoirs of limestone and sandstone formations are contaminated by a chloride brine (Mironenko and Rumynin 1999). The saturation of solution with the dissolution products of soluble minerals of the rock-matrix and the products of ion-exchange reactions may be high enough to practically suppress the adsorption of radionuclides. In particular, Sr-90 begins to behave similarly to a *nonreactive chemical* and migrates at the groundwater velocity. This conclusion is related to one of the most acute problems of environmental hydrogeology, namely, the problem of a “fast transport” of Sr-90 in subsurface environments. The “fast transport” of Sr-90 is of great practical interest for forecasting the propagation of dissolved radioactive materials in groundwater.

23.1.4 On the Direction of Processes Under Extremely High Temperatures

Actually, the transformations of the system taking place under high temperatures and pressures near injection wells at Tomsk-7 RW disposal site can have a more complex character determined by *transformations of the mineral phase of sediment*, as is confirmed by experimental data (Zakharova et al. 2005; Kaimin et al. 2008).

23.1.4.1 Tests with Acid Radioactive Solutions

The experimental series (Zakharova et al. 2005) involved experiments using samples of clayey sand with mineral composition close to that of sediment used in the above-described series (Table 23.2) with *acid solution* (pH = 1.3). The salt composition (gL^{-1}): $\text{NaNO}_3 = 94.7$, $\text{HNO}_3 = 2.16$, CH_3COOH (acetate) = 13.33, $\text{Fe} = 0.22$, $\text{Cr} = 0.57$, $\text{Mn} = 0.23$. The initial concentrations of radionuclides are as follows, BqL^{-1} : $\text{Cs-137} = 7.0 \cdot 10^5$, $\text{Sr-90} = 11.3 \cdot 10^5$, $\text{Pu-239} = 10.7 \cdot 10^5$, $\text{Np-237} = 2.0 \cdot 10^5$, $\text{Am-241} = 0.7 \cdot 10^5$, and $\text{U-238} = 0.05 \cdot 10^5$; $T = 150^\circ\text{C}$, $P = 3 \text{ MPa}$. The phase concentration ratio $L : S = 5 : 1$. The total duration of the experiment was about 50 days.

Analysis of experimental data shows that the thermolysis, radiolysis, and interaction with the mineral phase caused pH to increase to 3.4 by the end of experiment. At the same time, the concentrations of principal (“petrogenic”) cations was gradually increasing (Fig. 23.11a). Such changes are accompanied by transformations of minerals; in particular, in experiments, individual mica grains were seen to turn into minerals belonging to chlorite group, and some feldspar grains were coated by newly formed hydromica and montmorillonite. The result of these processes was an increase in the number of cationic functional groups contributing to an increase in sediment sorption capacity.

The passage of cations of the group of “technogenic” metals (Fe, Cr, Ni, Mn, Fig. 23.11b) from solution onto the sediment leads to the *formation of hydroxide films* on the surface of original and newly formed minerals; Fig. 23.11b, does not show the curve for Fe since the removal of this component from solution takes place within the first day. Studying the sediment with scanning electron microscope (Hitachi NSM-2a), has shown that hydroxide films of iron and chromium cover an appreciable portion of quartz grain surface. The role of films, serving as a technogenic geochemical barrier, which restricts the mobility of some radionuclides, was also mentioned in many previous studies. As follows from Fig. 23.11, the processes

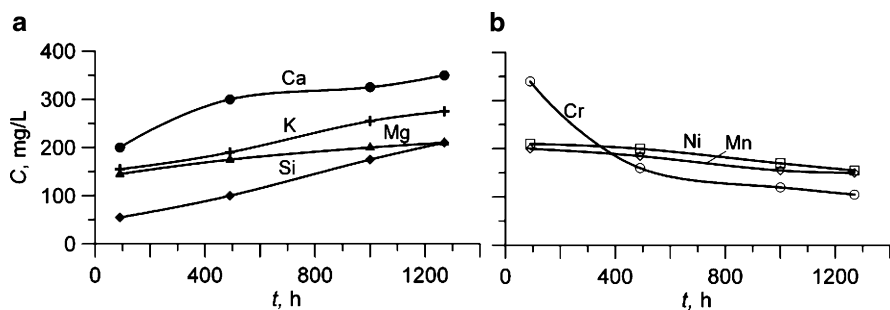
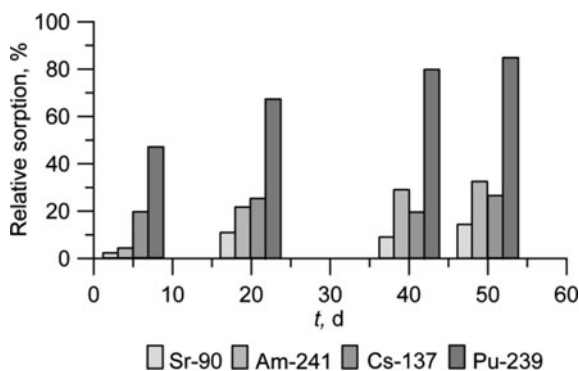


Fig. 23.11 Geochemical changes in solution in contact with sediment (at $T = 150^\circ\text{C}$ and $P = 3 \text{ MPa}$). Concentrations: (a) principal cations (Si, K, Ca, and Mg); (b) trace metals (Cr, Ni, and Mn)

Fig. 23.12 Plot of relative adsorption of radionuclides on the sediment (Zakharova et al. 2005)



mentioned above have a distinct kinetic character: the equilibrium in the system has not been attained within a sufficiently long experimental period (50 days).

The increase in sorption capacity accompanying the transformations of mineral phase at high temperature is confirmed by measurement data of radionuclide concentrations in liquid phase. These measurements allowed us to evaluate the percentage of radionuclides (relative adsorption) adsorbed by sand at different moments (Fig. 23.12). As can be seen, actinides (Pu-239 and Am-241) are the most sensitive to the kinetic transformation of rock mineral phase, and plutonium adsorption is appreciably greater than that for other radionuclides.

23.1.4.2 Tests with Alkaline Radioactive Solutions

The second series of experiments (Kaimin et al. 2008) was carried out at the initial value of pH 12.5. The salt composition of solution (gL^{-1}) was as follows: $\text{NaNO}_3 = 44.3$; $\text{Na}_2\text{CO}_3 = 2.1$; $\text{NaOH} = 10.8$; $\text{Al}^{3+} = 0.83$. The experiments were carried out with both dynamic and static regimes. Under dynamic regime, the temperature range 70–100°C was examined (with a duration of 42–84 days), while the temperature of 150°C was studied under static conditions (90 days). Quartz dominates in the initial phase of sand–clay rocks (averaged sample from well N17); other minerals form the following series by descending mass fracture: montmorillonite and kaolinite, feldspars, muscovite and biotite, chlorite, siderite. Many minerals occur in an altered state.

The experimental impact of an alkaline salt-containing solution at temperature of 70–150°C and pressure of 3 MPa causes the following transformations in minerals (Kaimin et al. 2008). At 70°C, newly formed montmorillonite with higher sodium concentration replaces feldspars, chlorites, and biotites. Also found was a newly formed mineral, which featured aluminum-to-silicon ratio intermediate between montmorillonite and kaolinite and higher concentrations of iron, magnesium, calcium, and sodium. Zeolites form at 70–100°C, which almost completely replace kaolinite in the rear zone (experiments under dynamic conditions). Moreover, at 100°C a newly formed phase was detected with the composition close to analcime (a feldspathoid) and the structure close to zeolites. At 100°C, the mineral

composition of sediment contains a newly formed phase, which can be referred to analcime in terms of both composition and the form of occurrence. This phase replaces kaolinite and partially forms over feldspars, micas, and chlorites or forms fringes around quartz grains. At all temperatures, magnetite and sodium carbonate salt forms as an independent phase or over montmorillonite.

The hydrolysable cations (Fe, Al) released during transformations in the system, as well as poorly soluble carbonate compounds and silicon dioxide precipitate on the surface of mineral grains, the possible result being changes in its sorption potential.

Under dynamic conditions, cation leaching leads to accumulation of Ca, Mg, Sr, and K cations near the replacement front: the plots of breakthrough concentration functions, C_i , constructed for such cations in coordinates $C_i - \bar{V}$ ($\bar{V}$ is the dimensionless number of pore volumes that have passed through the sample), look like the plots obtained under static conditions during step-by-step washing of samples (Fig. 23.1) and like the dynamic curves that are obtained by monitoring the fronts of motion of nitrate (Fig. 15.6c) or chloride salt fronts in groundwater pollution areas (Mironenko and Rumynin 1999; Rumynin et al. 2005).

Further, the sorption of U-233, Np-237, Pu-239, and Am-241 on the initial and transformed sediment was studied. To determine the occurrence forms of adsorbed radionuclides and to establish the sorption mechanisms, the selective desorption method was used (see also Sect. 19.1.2). It was established that after the interaction with hot solutions, the amount of exchange centers for uranium and neptunium decreases, i.e., it is likely that the appearance of newly formed montmorillonites and zeolites plays lesser role than the screening of active centers of minerals in the initial state. At the same time, the share of uranium and plutonium involved in reactions of surface complex formation and the share of these radionuclides irreversibly adsorbed by clayey sand increases. In the case of plutonium and ameritium, the amount of exchange centers on the transformed solid phase increases appreciably; the characteristics of the presence of tightly bound forms of these radionuclides remain about the same. Overall, the anthropogenic transformations of sediment facilitate the more complete adsorption of the examined radionuclides (Kaimin et al. 2008).

23.2 The Influence of Mineral Transformation of Aquifer Matrix on Radionuclide Sorption in Batch Tests with Core Material from the Krasnoyarsk-26 Site

23.2.1 General Information

The Krasnoyarsk-26 deep-well injection site is a part of an industrial complex (plant) for plutonium and enriched-uranium production, located on the eastern side of the Yenisei River, about 40–50 km northeast of the city of Krasnoyarsk (the eastern edge of the West Siberia Basin).

Deep-well injection has been ongoing at the Krasnoyarsk-26 site for more than 40 years, starting from 1967 (Compton et al. 2000; Rybalchenko et al. 2005). The total volume of RW injected by the early 2000s is 6 million m³ (Rybalchenko et al. 2005). Nowadays (2005–2010), the mean annual injection volume is about 100 thousand m³, of which the major portion (up to 80%) of the injected solutions is low-level RW (LLW).

The wastes are injected into two isolated aquifers confined to a trough-like structure and lying at depths of 400–480 m (low horizon, I) and 140–230 m (upper horizon, II) from the land surface. The injection of process solutions is accompanied by pumping out of equivalent formation water volume from relief wells. The hydraulic conductivities of sand deposits vary within a wide range from 1–1.5 md⁻¹ to tenths and hundredths fractions of meter per day. The total porosity is 0.2–0.3 (Compton et al. 2000).

Infiltration type of water exchange with downward groundwater motion within water divide zones of infiltration recharge and upward motion in discharge zones (river valleys) is characteristic of the site area. Groundwater flow velocities reach several meters per year (Compton et al. 2000). The waters in the aquifers are fresh (with TDS generally not exceeding 700 mgL⁻¹), weakly alkaline, hydrocarbonate, with complex cation composition.

The injected RW contain short-lived beta- and gamma-emitting radionuclides. According to the accepted safety strategy, the RW must remain isolated from the surface environment for at least 1,000 years. HLW and ILW are injected into the lower aquifer (Horizon I), and LLW into the upper aquifer (Horizon II). The total present-day activity of the waste stored in both horizons is estimated to be about 450 million Curies (MCi). As in the Tomsk-7 site, radioactive decay of short-lived radionuclides results in the heating of the recharged horizons.

23.2.2 Experimental Setup and Analysis of the Major Results

The major purpose of the experimental work was to assess how much the rock matrix's mineral transformations influenced its capability to retain radioactive waste components.

Samples of the clayey sand were taken from Horizon I. The mineral composition of the sand includes quartz, feldspar, biotite, muscovite, chlorite, illite, and kaolinite. The synthesized alkaline waste (representative of the predominant type of the radioactive waste injected in the subsurface) consists of NaOH (10.5), NaNO₃ (44.5), and Na₂CO₃ (2 gL⁻¹), with pH > 13. Batch experiments were performed in autoclaves under different temperature and pressure conditions (Tables 23.8 and 23.9). The liquid-to-solid phase ratio (L:S) in different experimental series was also varied, with the weight of each sample equal to 1 g. Quenched solutions and sand samples were examined to determine changes in the composition of liquid and solid phases. Radionuclide concentrations were determined by the radiometric technique.

Table 23.8 Changes in the composition of solution in batch experiments under different conditions (samples from the Krasnoyarsk-26 site)

Experimental conditions				Dissolved solids, mgL ⁻¹			
L:S	T, °C	Pressure, MPa	t, hr ^a	Al (±2%)	Si (±5%)	K (±5%)	Ca (±2%)
10:1	70	3.0	100	1.27	2.67	0.25	0.003
20:1	70	3.0	200	7.41	8.17	1.51	0.008
30:1	70	3.0	300	18.52	9.99	2.20	0.002
10:1	70	3.0	500	1.38	2.80	0.24	0.003

^aDuration of the experiment**Table 23.9** Sorption characteristics from the batch experiments (L : S = 10 : 1), the Krasnoyarsk-26 site

Radio-nuclide	Experimental conditions	Initial concentration, BqL ⁻¹	Equilibrium concentration, BqL ⁻¹	Percent of sorption, %	K _d , cm ³ g ⁻¹
Sr-90	20 °C, 0.1 MPa, 100 hr ^a	1.3 × 10 ⁶	1.9 × 10 ⁵ –1.5 × 10 ⁵	85.5–90.0	60–80
	70 °C, 3 MPa, 100 h	1.3 × 10 ⁶	6.5 × 10 ⁴ –5.9 × 10 ⁴	95.0–95.5	190–210
	70 °C, 3 MPa, 500 h	1.3 × 10 ⁶	6.8 × 10 ⁴ –5.9 × 10 ⁴	95.2–95.5	200–210
Cs-137	20 °C, 0.1 MPa, 100 h	5.3 × 10 ⁶	4.0 × 10 ⁵ –3.4 × 10 ⁵	92.5–93.5	120–145
	70 °C, 3 MPa, 100 h	5.3 × 10 ⁶	2.1 × 10 ⁵ –2.0 × 10 ⁵	96.0–96.2	240–250
	70 °C, 3 MPa, 500 h	5.3 × 10 ⁶	2.1 × 10 ⁵ –2.0 × 10 ⁵	96.0–96.2	240–255
Pu-239	20 °C, 0.1 MPa, 100 h	1.28 × 10 ⁶	6.4 × 10 ⁴ –5.0 × 10 ⁴	95.0–96.0	200–240
	70 °C, 3 MPa, 100 h	1.28 × 10 ⁶	2.5 × 10 ⁴ –1.3 × 10 ⁴	98.0–99.0	500–970
	70 °C, 3 MPa, 500 h	1.28 × 10 ⁶	1.3 × 10 ⁴ –6.4 × 10 ³	99.0–99.5	1000–1300
Am-241	20 °C, 0.1 MPa, 100 h	1.1 × 10 ⁵	5.2 × 10 ³ –5.0 × 10 ³	95.2–95.5	200–210
	70 °C, 3 MPa, 100 h	1.1 × 10 ⁵	2.2 × 10 ³ –1.1 × 10 ³	98.0–99.0	500–950
	70 °C, 3 MPa, 500 h	1.1 × 10 ⁵	1.1 × 10 ³ –5.0 × 10 ²	99.0–99.5	980–1200

^aDuration of the experiment

Table 23.8 lists the observed changes in the composition of the waste after contact with sand samples at elevated temperature and pressure. It appears that the exchangeable and petrogenetic cations (composing the minerals) were leached out of

the mineral phase. The observed concentrations depend on the L:S ratio rather than the duration of the experiments. The results of the batch experiments indicate that at elevated pressure and temperature, noticeable amounts of aluminum, silica, and (to a lesser extent) potassium were leached from the rock matrix. In contrast to the acid-waste experiments (samples from the Tomsk-7 site), calcium was observed in the trace-level concentrations.

A similar set of experiments was performed under room conditions ($T = 20^{\circ}\text{C}$, $P = 0.1\text{ MPa}$). It was found that solution's general tendency in component accumulation remained the same; however, the leaching process intensity was observed to be much lower.

The tested samples of the sand were also subjected to a visual, microscopic examination to estimate the alteration in the mineral composition of the sediment. It was revealed that when a solid material is dissolved by interacting with hot alkaline solution, new mineral associations precipitate under room conditions. The predominant neogenic amorphous form is aluminum hydroxide coating mica minerals (in particular, biotite); some inclusions of aluminum hydroxide may be observed within the mica cleavage.

In the batch experiments, the apparent phase distribution coefficients under different experimental conditions were evaluated (Table 23.9). Table 23.9 indicates that the higher the temperature and pressure, the greater the values of the sorption distribution coefficient, K_d . The radionuclide sorption also depends on the chemical properties of the elements, particularly their capability for hydrolysis in the alkaline solution. In our case, actinides (such as Pu-239 and Am-241) are most liable to the hydrolysis. Therefore, the rise of the distribution coefficient values can be explained by actinide co-precipitation with hydroxyl aluminum in the porous matrix. Co-precipitation of Pu-239 with silicate minerals is also possible.

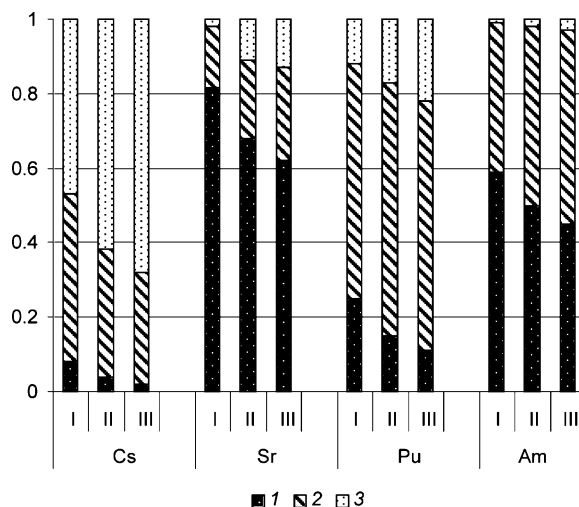
Desorption of radionuclides in the process of washing (successive desorption technique) sand samples with different solutions was studied (Sabodina et al. 2008): (1) water and a dilute solution of ammonium acetate (1 M, pH 4.8); (2) hydrochloric acid (1 M); and (3) hot (90°C) hydrochloric and nitric acids (6.0–7.5 M). The percentage of the radionuclides removed from the mineral phase by washing the samples with the three types of solutions can be conditionally associated with the quantities in the solid phase of (1) mobile, (2) medium-mobility, and (3) low- (poor) mobility radionuclides. The results of experiments are presented in Fig. 23.13.

From the results of the selective desorption, the following conclusions can be derived.

Cesium-137. A major fraction of Cs-137 is incorporated into the mineral structure, and the radionuclides are basically leached from the sediment when matrix dissolution occurs; Cs-137 is partly absorbed by the hydroxide metals comprising the neogenic films. The percentage of Cs-137 in the ion exchange complex is negligible. Also, with an increase in temperature and rock-waste contact time, the amount of the low-mobility species increases.

Strontium-90 is a relatively mobile and exchangeable species. Sr-90 is partly absorbed by the neogenic films and by carbonate minerals. The percentage of the

Fig. 23.13 Diagram illustrating different radionuclide mobility. (1) Mobile, (2) medium-mobility, (3) low-mobility. (I, II, III) Experimental conditions: (I) $T = 20^{\circ}\text{C}$, $t = 100\text{h}$; (II) $T = 70^{\circ}\text{C}$, $t = 100\text{h}$; (III) $T = 70^{\circ}\text{C}$, $t = 500\text{h}$



low-mobility species is low, but increases with rising temperature. In this respect, the behavior of Sr-90 is the opposite of that in acid solutions (compared with experiments with sands from the Tomsk-7 site).

Americium-241 can be considered a mobile, exchangeable species; it is absorbed by neogenic films and carbonate minerals in approximately equal parts. An increase in the rock-waste contact time results in a decrease in the quantity of Am-241 sorbed by the films, probably due to a transformation in the structure and a change in the properties of the films. The percentage of the low-mobility species does not exceed 2%.

Plutonium-239. In comparison with americium, Pu-239 is less mobile; it is absorbed by the films, clay, and sand grains. The low mobility fraction ranges up to 10–15% and increases with rising temperature.

Only the water-soluble or ion-exchangeable radionuclides can be desorbed quickly from the sediment under natural attenuation when groundwater flows through the contaminated sediment. Based on the represented results, we can establish a mobility sequence for the radionuclides under consideration, the most mobile being Sr-90, followed by Am-241, Pu-239, and Cs-137.

In conclusion, we give some results of dynamic (flow) experiments with clayey sand of the same complex (Kaimin et al. 2004). As well as in the experiments described above, heated (to $T = 70^{\circ}\text{C}$) alkaline radioactive solution “on sodium base” was used (gL^{-1}): $\text{NaNO}_3 = 44.3$, $\text{Na}_2\text{CO}_3 = 2.1$, $\text{NaOH} = 10.8$. The examined radionuclides were represented by Sr-90, Cs-137, and Pu-239. The major mineralogical and chemical transformations of the aquifer material took place near the inlet boundary of the flow: the shares of the initial minerals have changed and new minerals have formed. Thus, a new mineral, belonging to the zeolite group (most likely, natrolite with higher iron and lower sodium) has formed in the rear part of the sample. This mineral almost completely replaces kaolinite and, instead of it,

Table 23.10 The amount of different forms of radionuclides (%), adsorbed on the initial and treated clayey sand samples

Nuclide forms	Sr-90		Cs-137		Pu-239	
	I ^a	II ^b	I	II	I	II
Water-soluble	1	1	2	6	8.5	4.5
Exchange	79	66.5	8.5	0.5	27.5	3
Mobile	15	15	10.5	6.5	10.5	1.5
Low-mobility	5	17.5	79	87	53.5	91

^aFresh sediment

^bSediment with transformed mineral matrix

cements other minerals. Minerals of montmorillonite group form in the central and frontal zones of the sample. Biotite and chlorite are destroyed in this process. No pure montmorillonite was detected in the rear zone.

Such transformations have a considerable effect on sediment sorption capacity, as can be seen from the analysis of Table 23.10, containing data on selective desorption of radionuclides adsorbed near the rear boundary of the flow. The obtained results (Kaimin et al. 2004) show that: (1) Sr-90 occurs mostly in exchange form; low-mobility forms are few, though their amount increases in the case of sorption on treated sediment; Cs-137 occurs in low-mobility forms, whose amount increases after filtering of an alkaline solution (in a transformed sediment); (3) in the case of sorption of Pu-239 on a treated rock, the amount of all typical forms able to migrate decreases; (4) clearly, the formation of zeolites facilitates an increase in the sorption of this actinide by the rock.

Thus, the materials given here suggest that active mineralogical transformations that change the conditions of sorption interaction between the rock and radionuclides take place in the aquifer in the zone of radioactive waste migration. This is in agreement with the general knowledge of metamorphism processes in natural systems. In particular, the injection of alkaline RW leads to montmorillization of the clayey rock component and accumulation of hydromicas takes place. During the injection of acid solutions, physicochemical transformations facilitate the kaolinization of minerals. The development of migration models that take into account the technogenic mineralogical transformations facilitated by live microorganisms or their metabolites is an acute problem in hydrogeology and radiogeoeology.

The transformation of some minerals into others can be accompanied by a release of mineral particles into the liquid flowing in rock (sediment) pores. The latter are potential carriers of radionuclides adsorbed on their surface (see Part IX).

23.3 Radionuclide Sorption onto Fresh Fractures of Volcanogenic Metamorphized Rocks from the Lake Karachai Site

The conditions of groundwater pollution by radioactive brine (ILW) at the Lake Karachai site has been described in details in Chap. 15. It was noted that the behavior of radionuclides is governed by the presence in water and liquid RW of various

dissolved forms of other components and complex particles. Therefore, strictly speaking, forecasting radioactive pollution of groundwater in the area requires the application of transport models accounting for the multi-component and multi-site nature of the system. However, approximate estimates can be obtained based on K_d -concept (see Sect. 20.1.1.2), which takes into account possible variations in the sorption distribution coefficient in the fractured medium, K_a , depending on the average composition of solution.

Indeed, the mass-transport potential is determined mostly by the bulk salt flux, which is characterized by the current content of the total dissolved solids and solution density. The concentration of sodium nitrate, NaNO_3 , which dominates in the liquid RW and correlates with its density, can therefore serve as a major potential-specifying function for radionuclides affecting the overall transport potential.

On the other hand, the behavior of radionuclides is governed by the concentration distribution of many other dissolved components and complexing species. Therefore, predicting the fate of the radionuclides requires the use of reactive solute transport models. A simplified analysis can be based on a “ K_d approach,” taking into account the variability of coefficients of equilibrium distribution.

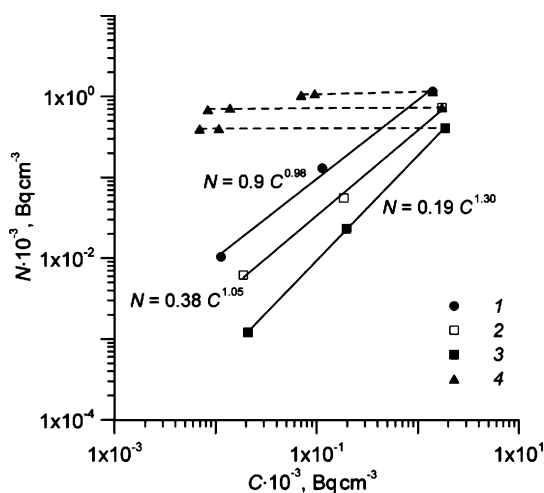
23.3.1 Samples and Experimental Setup

A set of sorption (adsorption) experiments has been carried out for studying Sr-90 sorption onto fracture surfaces (Rumynin et al. 1998). Three major aspects of the problem have been evaluated: (1) the types of sorption–desorption isotherms; (2) the influence of NaNO_3 concentration on the coefficient of equilibrium distribution, K_a , at sorption and desorption stages; and (3) the irreversibility of the sorption process.

Core materials were taken from three different boreholes in uncontaminated areas, within separate depth intervals (Table 23.11). The samples are represented by welded tuffs, scoriaceous lavas, tuffs, and tuff breccias moderately metamorphosed into greenschist facies. The core samples were cut into disc-shaped wafers (up to 90 mm in diameter and 2–4 mm thick). Sets of discs were placed into glass containers filled with NaNO_3 solutions containing Sr-90. Three basic concentrations, C_s , of NaNO_3 were selected for creating the hydrogeochemical environment related to the site under consideration: 1, 15, and 70 gL^{-1} . This gradation corresponds to the typical hydrogeochemical zones of groundwater contamination. For the desorption step, the solutions were replaced by background (uncontaminated) water. After a special series of experiments, it was established that a period of about 100 h is sufficient to attain chemical equilibrium between liquid and solid phases during adsorption and desorption stages.

Table 23.11 Characteristics of studied rock samples (from the Lake Karachai site) and calculated values of the equilibrium distribution coefficient

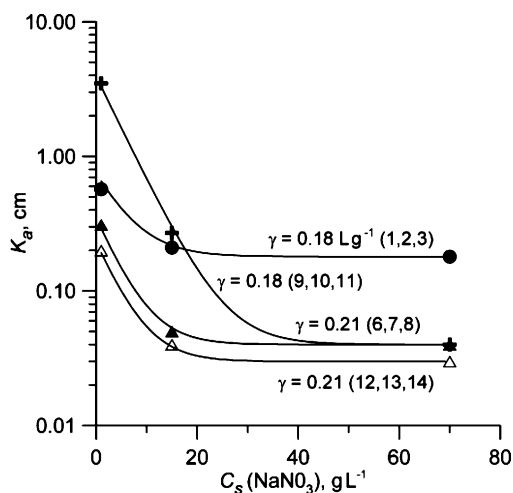
Rock	Borehole	Interval, m	Experiment	NaNO ₃ , gL ⁻¹	K_d^s , cm	K_d^d , cm
Tuf-and-lava	1–96	98–100	1	1.0	0.57	1.54
			2	15.0	0.21 ^a	1.0
			3	70.0	0.18 ^a	11.7
Tuf-and-lava	1–96	16	4	1.0	1.89	12.8
Lava breccias	8002	690	5	1.0	0.57	1.85
Tuf-and-lava	1–96	71	6	1.0	0.31	2.9
			7	15.0	0.05	4.1
			8	70.0	0.04	6.6
Tuf	1–96	26	9	1.0	3.49	436
			10	15.0	0.27	99
			11	70.0	0.04	69
Lava breccias	211	–	12	1.0	0.20	2.0
			13	15.0	0.04	9.1
			14	70.0	0.03	9.1

^aDesorption under constant NaNO₃ content**Fig. 23.14** Sorption isotherms (borehole 8002, depth 938 m) and desorption points. (1, 2, and 3) Sorption from solution, $C_s = 1, 5$ and 70 gL^{-1} . (4) Desorption

23.3.2 Sorption Parameters

Figure 23.14 illustrates an example of sorption isotherms obtained for samples taken from one of the boreholes. It has been observed that the equilibrium relationship between Sr-90 concentrations on the surfaces of the discs and in liquid phases are nearly linear for $C_s = 1$ and 15 gL^{-1} . An increase in NaNO₃ content in the solution leads to a shift of adsorption into a nonlinear field. Unfortunately, experimental data for a comprehensive isotherm-based analysis of the sorption process are limited;

Fig. 23.15 The influence of NaNO_3 content on the distribution coefficient (theoretical curve calculations are based on Eq. 23.2; the numbers of samples (Table 23.11) are shown in brackets)



therefore, for further analysis, data on the values of the apparent phase distribution coefficient K_a (Table 23.11) will be mostly used.

The values of K_a depend strongly on the concentration of sodium nitrate: the more dilute the solution, the greater the value of K_a . In the majority of the experiments with highly concentrated solutions (70 gL^{-1}), the values of K_a were found to be less than 0.04 cm . In the diluted solutions (1 gL^{-1}), the values of K_a are at least 5–10 times greater.

The relationship between K_a and NaNO_3 content, C_s , can be approximated by the following equation:

$$K_a = K_{a1}e^{-\gamma C_s} + K_{a2}, \quad (23.2)$$

where the sum of K_{a1} and K_{a2} corresponds to the coefficients of sorption in diluted solutions, and K_{a2} in concentrated solutions. The average value of γ is 0.2 Lg^{-1} (Fig. 23.15).

23.3.3 Hysteresis in Sorption

The phenomenon was studied in the process of step-by-step desorption of previously adsorbed Sr-90; at the end of each desorption step, the radioactive solution was replaced by radioactivity-free water. The measured concentration points at the sorption and two-step desorption stages of the laboratory experiments for two sets of experiments are depicted in Fig. 23.14. Analysis of the experimental results shows that all desorption concentration points are located above the sorption isotherms.

Furthermore, it was established that the desorption coefficients K_a^d , calculated according to the traditional balance approach (Vandergraaf and Abry 1982;

Wels et al. 1996), significantly exceed the sorption coefficients $K_a^s \equiv K_a$ (Table 23.11): the greater the concentration of NaNO_3 in the solution at the adsorption stage, the greater the calculated ratio K_a^d/K_a^s . This means that the desorption of radionuclides initially adsorbed in a high-concentration solutions is limited.

The results of multistep desorption experiments showing differences between K_a^s and K_a^d can be explained in the light of the previous analysis of experiments with unconditioned sands from the Tomsk-7 site. Thus, the variability of the hydrogeochemical environment at different stages of the tests is responsible for the nonsingular process.

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Part IX

Colloid-Facilitated Solute Transport in Aquifers

Starting from the mid-1980s, an avalanche of publications has appeared, generalizing studies of different aspects of the effect of colloids on the migration capacity of dissolved pollutants, primarily, radionuclides. The major attention is paid to the development of solute transport models incorporating the mechanisms of sorption of contaminants (e.g. actinide ions such as Pu-239, Np-237, Am-243) or intrinsic colloids onto mobile aquatic nm-size particles, which are composed of inorganic or organic water constituents and referred to *pseudocolloids*. This phenomenon and this form of mass transfer in groundwater will be the main topic of the following sections of this book. The obtained results suggest, as a rule, that colloidal particles are potential vehicles for the contaminant species commonly referred to the class of strongly sorbing (actinides, first of all). Therefore, contaminants adsorbed (especially irreversibly) onto pseudocolloids can be transported over considerable distances with velocities close to pore velocity of the formation water. The larger colloids exhibit little retardation in fractured-porous reservoir because their size prevents them from entering the wall-rock pores (Moridis et al. 2001) and matrix diffusion cannot perform the retention function protecting groundwater against contamination. Thus, the manifestation of this mechanism increases the groundwater pollution hazard.

Less definite is the role in migration processes of *intrinsic* or *real colloids*, mostly generated by the products of actinide hydrolysis through oxo and/or hydroxyl bridge formation (Zhao and Steward 1997; see also Sect. 25.1). It is only clear that the presence of colloids in groundwater can increase the total concentrations of actinides above the equilibrium thermodynamic solubility limits, and thereby increase the mass amount of actinides transportable to the environment.

The significance of colloid transport increases in the case of (1) the presence in the pollution source of very toxic substances (components) with low Safety Standard Permissible Values (e.g., actinides), such that the transport of these substances in aquifers in ultra-low concentrations can have a significant effect on the radioecological conditions of water; (2) sufficient mobility of colloidal particles; (3) the formation of strong physicochemical bonds between colloids and dissolved matter (at slow desorption kinetics). The latter is the cause of a paradoxical situation, which

is typical, for example, of actinide-containing solutions: the higher the adsorption characteristics, the greater the potential hazard of a large-scale pollution of aquifers and the less favorable the estimates of their impact on groundwater.

The problem of colloid-facilitated solute transport has several aspects: (1) the nature (origin) of colloidal particles, their composition and properties; (2) the migration capacity of colloidal particles; (3) the formation of chemical bonds allowing colloids to retain components on their surface; (4) migration of colloid-containing solutions in different types of groundwater reservoirs analyzed with allowance made for possible changes in the physicochemical conditions over space and time.

In this study, we analyze the current state of the problem and develop model (theoretical) descriptions of the migration process, supplemented by analysis of experimental material from Tomsk-7 site, associated with deep-well disposal of RW in a geological formation.

Chapter 24

Colloidal Systems and Equilibrium in Such Systems

In this chapter, primary factors controlling the stability of colloidal systems and adsorption-related interactions of colloidal particles with dissolved chemical species are considered. Governing equations for sorption equilibrium and kinetics are formulated. A number of case study researches elsewhere illustrating the presence of colloids in groundwater at different locations and their role in the trace element (in particular radionuclides) binding and capture within this environment are examined. All this creates a basis for the further development (Chaps. 26 and 27) of colloid-facilitated transport models.

24.1 General Views on Colloids and Their Genesis

Colloids are very fine particles that range in size between 1 and 1000 nm and have high, size-dependent, specific surface area. The particles collectively represent the disperse phase, intermediate between the solution, in which dissolved particles have the size of the order of an angstrom and particles more than 1 nm in size, which can physically adsorb matter from solution and precipitate under the effect of gravity. In other words, colloid populations represent a “third phase”, which is neither liquid, nor solid.

In equilibrium systems, where the appearance of colloids is associated with chemical weathering of rock formations during their interaction with groundwater, the distribution of colloidal particles over size can be described by Pareto’s power law (Degueudre et al. 1996a, b; Kretzschmar et al. 1999):

$$\frac{d(C_{\text{coll}}^{\text{pt}})}{d(d_{\text{coll}})} = A d_{\text{coll}}^{-b}, \quad (24.1)$$

where A and b are constants (under idealistic conditions, b value is close to 4); d_{coll} is the size (nm); $C_{\text{coll}}^{\text{pt}}$ is an accumulated concentration (the number of particles per ml) of colloids with size d_{coll} . When $b > 1$, and the size of particles is

continuously distributed within the range from $d_{\text{coll}}^{\text{m}}$ (minimal value) to $d_{\text{coll}}^{\text{M}}$ (maximal value), the accumulated concentration can be explicitly found by integrating the relationship (24.1):

$$C_{\text{coll}}^{\text{pt}} = \frac{A}{b-1} \left[(d_{\text{coll}}^{\text{m}})^{1-b} - (d_{\text{coll}}^{\text{M}})^{1-b} \right]. \quad (24.1a)$$

In practical calculations, the minimal value d_{c}^{m} is taken to be the lower sensitivity limit of experimental measurements, and the maximal value is related to the limit corresponding to the presence in water of large-diameter particles in insignificant concentrations.

This general validity of Pareto's law implies that in most water samples, the number of small particles may be orders of magnitude greater than the larger ones, e.g., 10^6 times more 10-nm particles than 1- μm particles (Buffle and Leppard 1995). The size distribution based on particle mass gives a completely different picture: the mass proportion of small particles is much smaller than that of the larger ones (Buffle and Leppard 1995). Size distributions based on number and mass are thus complementary representations.

Available experimental data also indicate that colloids found in natural environments typically may follow a lognormal distribution in size (diameter) (Groffman and Mejer 1993; Ledin et al. 1994). James and Chrysikopoulos (1999) have shown that variability in particle size may affect transport properties of colloid systems.

The character of distributions also depends on the composition of solution. Thus, the concentration of Ca^{2+} ions was found to affect the size distribution of colloids (Fujita et al. 2003). Obviously, polydisperse character of colloid suspensions must affect the potential of contaminant transport in groundwater. This is accounted for by the existence in a single colloidal population of particles with different adsorption capacity, thus carrying different amounts of contaminants (Sects. 26.1.2 and 26.3.2).

Overall, the chemical composition, structure, and size of colloids may vary within a wide range, depending on the hydrochemical conditions in groundwater.

Colloids may have:

- (1) natural origin, i.e., occur in groundwater in background concentrations as the result of natural processes of physicochemical weathering of sediments and rocks (in situ mobilization processes are the main source of colloids);
- (2) artificial origin, caused (i) by the destruction of cement (clay) material – engineering barriers isolating radioactive waste repositories from the geological environment and biosphere, (ii) generation of colloids due to the interaction between migrating solutions and soils, unsaturated geological media or aquifer materials, (iii) generation in liquid phase oversaturated with a soluble salt.

The most typical representatives of *natural colloids* are high-molecular organic compounds (acids), aluminosilicates, oxides and hydroxides of iron and aluminum, and metastable ferrohydrates. Colloids can form from oxides and hydroxides of actinoids, such as U, Np, and Am. Again, there exist “biocolloids,” represented by microorganisms (bacteria and viruses), which are also potential carriers of contaminants (Runde 2000; McCarthy and McKay 2004).

The mean concentrations of colloids in fresh groundwater are generally $< 1\text{ mg/L}$, though natural solutions with colloidal particle concentrations up to several tens of milligram per liter can be met. The number of colloidal particles per liter varies from 10^8 to 10^{17} (Kim 1990). Higher concentrations of colloids are typical for aquifers with higher dissolved organic matter concentrations.

Thus, the mean variation range of colloid concentration in fresh groundwater near the proposed Yucca Mountain Nuclear Waste Repository site, Nevada, USA, is $0.3\text{--}0.7\text{ mg/L}$ (some samples show higher concentrations, such as 6.25, 25, and 145 mg/L ; Contardi et al. 2001). The number of colloidal particles varies in this case from $1.05 \cdot 10^9$ to $2.72 \cdot 10^{13}$ particles/L. The same order of magnitude of concentrations was recorded in groundwater in crystalline rocks of Canadian Shield (Vilks and Baik 2001). Colloid concentrations of $4.3\text{--}63\text{ mg/L}$ (with particle diameter of $100\text{--}450\text{ nm}$) were recorded at the Nevada Test Site, USA (Buddemeier and Hunt 1988). Later studies, based on data of sampling of two wells in the zone of influence of underground nuclear explosions give the mean diameter of colloidal particles of $80\text{--}100\text{ nm}$ with their concentration in groundwater up to 0.25 mg/L (see also Sect. 24.4.1).

Similar concentrations of organic colloids, around $3.4 \cdot 10^{11}$ particles/L, were detected in groundwater near Gorleben site, Germany, which is planned to serve, with the salt dome Gorleben, as a future deep final repository for waste from nuclear reactors, and around $3.2 \cdot 10^{11}$ particles/L at Grimsel Test Site, deep underground rock laboratory in the Swiss Alps (Kim 1990). The high correlation between microcomponent concentrations and the total concentration of water-soluble organic matter, which was established by studies in Gorleben, serves as direct evidence of the potential capacity of organic colloids to transport radionuclides, in particular, actinoids (Kim 1990). Of particular interest is the fact that a linear correlation has been found to exist between the concentrations of organic substances and three- and four-valence heavy metal cations ($z \geq 3$), which can be considered as chemical analogues of actinides in aqueous solutions.

Detailed studies of the colloidal fraction of groundwater were carried out using samples taken at Grimsel Test Site (Degueldre et al. 1989, 1996a, b). Groundwater confined to a fractured rock massif contains on the average 0.1 mg/L of colloids ($d_{\text{coll}} = 10\text{--}1000\text{ nm}$), represented by silicon dioxide and phyllosilicate minerals; organic colloids occur in limited amounts. The parameters of distribution equation (24.1) are $A = 13.3 \pm 0.4$, $b = 4.2 \pm 0.2$.

Conversely, organic colloids (with a negative charge) are a dominating transport form of Pu(IV)-239/240 and Am-241 at Rocky Flats site, connected with nuclear weapon production facility near Denver, Colorado, USA (Clark et al. 2006, see also Sect. 24.4.1); nowadays, this plant is closed and the territory is under rehabilitation.

It can be seen that natural colloid system are often associated with natural organic matter (NOM), whose concentration in water is measured in mg C/L . NOM is a diverse mixture of organic compounds ranging from macromolecules to low-molecular-weight compounds such as simple organic acids and short-chained hydrocarbons. The molecular weight of organic molecules varies from 200 to $>10^5\text{ g/mol}$. The structure and composition of each organic component are also

very diverse. It is clear therefore that, the total concentration of NOM being the same, the properties of natural solutions in terms of their participation in physico-chemical interactions can be different. The total concentration of NOM in water in shallow aquifers generally does not exceed a few tens of mg C/L. The dominating size of organic colloids is 1–2 nm. An increase in dissolved salt concentrations can lead to aggregation of organic colloids, increasing their size to $N \cdot 10 - N \cdot 100$ nm.

Artificial (anthropogenic) colloids appear in groundwater during the decomposition of cement materials used to isolate radioactive waste. Commonly, these are bentonites.

According to experimental works (Fujita et al. 2003), the leaching of cement hydrates used to isolate RW leads to the formation of colloids of mostly Si, Ca, and Al composition. Colloid concentrations in this case reach $10^{11} - 10^{12}$ particles/L (at low S:L ratios of 1:50 and 1:100); a general trend was observed: the higher S:L ratio, the lower colloid concentrations and the larger the size of particles in colloid populations.

The corrosion of materials of containers used to store RW also contributes to the appearance in groundwater of colloids with mostly Fe(II/III) composition (Geckeis et al. 1998). Their concentration is controlled by the ionic strength of solution surrounding the containers and the ratio of the waste contact area to the liquid phase volume: the greater this ratio, the higher the colloid concentration in solution (Geckeis et al. 1998).

The processes leading to colloid formation through the interaction of moving polluted solutions with natural waters and sediments and rock materials are still not clearly understood. Analysis of the results of a few experiments shows, in particular, that the release of colloid particles from rock matrix depends on the composition of solutions (cations and organic and inorganic ligands) (Beretsch and Seaman 1999; Grolimund and Borkovec 2001a, b). The description of mobilization of colloid particles during groundwater motion can be based on phenomenological models (Grolimund and Borkovec 2001b). An increase in pH and (or) a decrease in the ionic strength of solution enhance the accumulation rate of colloids released from sand material samples (Crancon et al. 2001). Active colloid formation takes place during freshwater replacement from rock by brines.

A result of migration process can be the formation of colloids during the mixing and interaction between polluted groundwater with lower redox-potential and oxygen-containing waters. This takes place, for example, during the oxidation of ferrous iron, leading to the formation of ferrihydrous oxy hydroxides – dispersed colloids (Groffman and Mejer 1993). The formation of this type of iron and aluminum colloids with the size varying from 100 to 300 nm and the total concentration of about 1 mg/L was recorded during mixing of weakly acid mine waters (with low Eh) with near-neutral waters (with higher Eh) (Zänker et al. 2000). The influence exerted by the mixing processes taking place at the interaction front between the replacing and replaced solutions on colloid formation was mentioned in the study of Schäfer et al. (2000): the increase in the concentrations of inorganic colloids during the passage from oxidation to reduction conditions varied from 0.01 to 0.1–1.0 mg/L.

The change of the hydrochemical environment in the aquifer from oxidation to reduction commonly leads to the dissolution of feriferous oxy hydroxides in the cement material of the porous matrix. This material decomposes, adding clayey particles into porous water and increasing the mobility of the migrating solute (e.g., radionuclides).

24.2 Properties of Colloidal Systems

24.2.1 *Stability of Colloidal System*

Colloid populations in groundwater can be stable or unstable depending on particle properties and formation water chemistry. In unstable systems, colloidal particles agglomerate and may deposit due to gravitation. Coagulation-sedimentation processes depend not only on the physical properties of the colloidal material, such as size, density, compactness, but also on the chemical properties of the surfaces and ambient solution, which determine the strength of binding between the colloidal particles; electrical potential, chemical reactions as well as microbial activities are key processes for the production and degradation of colloids and macromolecules (Buffle and Leppard 1995).

The forces that allow particles to remain disperse are of electrochemical nature. These forces, measured in the laboratory, are a consequence of the charge on the surface of colloidal particles, e.g. most metal oxides have a surface layer of the metal hydroxide which is amphoteric and can become either positively or negatively charged (Sect. 27.1) by taking up a proton or by proton abstraction, depending on the pH. It can be seen that the charge can be either positive or negative, so the surface potential φ_p , may also have either sign. The electrostatic potential on the particle surface, relative to the surrounding fluid, is strongly dependent on the balance between the positive and negative ions, the *potential-determining* ions, in the solution. For oxide systems and many other colloids, H^+ and OH^- are potential-determining ions. In such systems, the surface charge and potential are determined largely by the balance between H^+ and OH^- in solution i.e. by the pH.

Electrostatic forces counteract the van der Waals attraction, which causes particles to stick to each other when they come within a few nm of each other. The van der Waals attraction arises from the fact that each atom in a particle exerts an attractive force on each atom in an adjacent particle.

Thus, the theory of colloid stability is based on the recognition of two forces in any stabilized solution: the electrostatic repulsion, which opposes aggregation, and a universal attractive van der Waals force, which acts to bind particles (within close enough contact) together. The theory is known as the DLVO theory after the four scientists (Deryaguin, Landau, Verwey, and Overbeek) who were responsible for its development (Kretzschmar et al. 1999; Allen et al. 2001; Fujita et al. 2003).

The magnitude of electrostatic potential depends on the thickness of the double electrical layer, which, in its turn, is controlled by the solution composition and ionic strength, I . In numerous studies (see, e.g., McDowell-Boyer et al. 1986; Fujita et al. 2003) the DLVO theory is used to calculate the total interaction potential of colloidal particles $\varphi_{\Sigma} = f(H)$, where H is the distance between particles. In the general case, at low values of I , the plots have a maximum associated with an energy barrier, which prevents the approaching of colloidal particles, i.e., aggregation. As the ionic strength increases, the peaks in the plots of $\varphi_{\Sigma} = f(H)$ disappear, i.e., the compression of diffusion layers reaches the values at which the attraction forces prevail at all distances H , i.e., coagulation of colloidal particles takes place.

Thus, during the leaching of hydrocements, containing Si-, Ca- and Al-colloids, the critical state of the system is associated with calcium ion concentration in solution near $1 \cdot 10^{-3}$ M: the system becomes unstable when this value is exceeded (Fujita et al. 2003). Experimental studies of colloid formation resulting from the decomposition and leaching of spent fuel elements and various insulation materials has also shown that the stability of colloid systems abruptly drops with an increase in the concentration of dissolved salts-NaCl and MgCl_2 (Geckeis et al. 1998).

Overall, as a coarse tentative estimate, we can assume that stable colloidal systems are associated with solutions where alkaline cations Na and K dominate and their concentrations are below 10^{-2} M, at the same time, the concentrations of alkaline-earth cations Ca and Mg should be below 10^{-4} M (McCarthy and Degueldre 1993). Groundwater of low ionic strength and high pH enhances colloid stability, as demonstrated in various laboratory and field experiments.

Thus, the ionic strength of solution is among the key factors that control the mobility of colloid fraction. While the particle agglomeration is a reversible process, the migration processes that reduce soluble salt concentrations in solution in moving hydrogeochemical systems (as takes place, e.g., on moving hydrogeochemical barriers) can facilitate re-immobilization of previously precipitated flocculus of colloids and their return into pore water.

Such effect was observed, for example, in migration experiments, when an abrupt drop in solution ionic strength caused re-immobilization of colloids, which accounted for the transport of 5–10% of uranium (Crancon et al. 2001). Under natural conditions, such direction of the process may lead to seasonal variations of uranium concentrations associated with variations in groundwater infiltration recharge at the annual scale (Crancon et al. 2001).

As was the case with colloids, the surface of the mineral phase also has surface charge and potential, φ_m . When colloids in groundwater have a charge opposite to that of mineral particles, the former will tend to attach to the latter due to electrostatic interaction. Otherwise, if the charges of colloids and mineral matrix have the same sign, mineral grains will repel colloids with the result that the velocity of their transport with water flow through the rock formation will increase.

The surface charge of colloids and mineral grains is governed by the interaction between dissolved components and surface functional groups (Sect. 27.1) on the surface of colloids and minerals. These surfaces are surrounded by double electric

layers interacting with formation water. The thickness of double layers depends on solution geochemistry, in particular, ionic strength. When ionic strength increases, the electric layers contract. This reduces the ability of colloids with identical charges to repel one another, resulting in agglomeration (coagulation or flocculation) of colloidal suspension and sedimentation of the newly formed agglomerates. The agglomeration of colloids in an aquifer may result in the formation of relatively large particles, which cannot move fast in the porous medium.

The effect of the ionic strength of solution on the activity of within-pore migration of colloid particles can be illustrated by the results of experiments in columns filled with porous material (Harmand and Sardin 1994). It was found that the increase in the ionic strength, which results in a compression of double electric layers, enhances the adsorption attachment of mobile particles to the mineral surface of sand material: with an increase in the concentration of NaCl solution from 10^{-4} to 10^{-2} M, the value of the dimensionless time ($\bar{t} = qt/L\phi$ or the number of pore volumes of the liquid that have passed through the column) when 50% concentration was recorded on the breakthrough curve increased more than threefold.

Figure 24.1 illustrates the manifestation of the attraction and repulsion forces in the interaction between spherical colloidal particles (1 μm in diameter) with a potential of $\varphi_p = -30\text{ mV}$ and a planar mineral surface with a potential $\varphi_m = -30\text{ mV}$ for ionic strength I varying within $10^{-4} - 1.0\text{ M}$. With the ionic strength of 10^{-4} M , thick double layers enhance the electrostatic repulsion, which dominates at distances from 0.3 nm (3 $\text{\AA}$) to 200 nm. In solutions with medium ionic strength, diffusion layers contract and a second-order minimum appears, where van der Waals attraction forces dominate over electrostatic repulsion forces. Nevertheless, the energy barrier still exists, preventing the particle from reaching the surface of mineral phase.

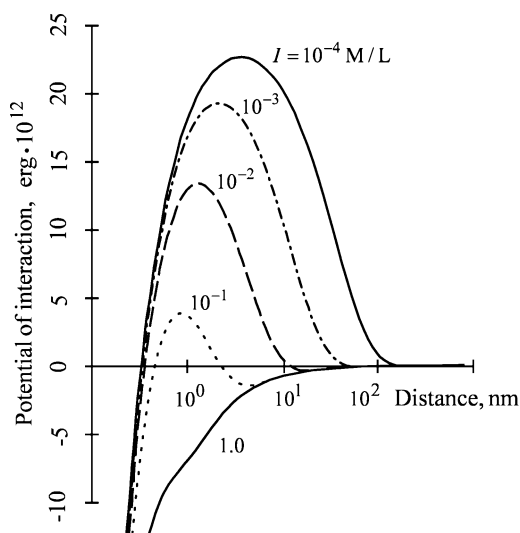


Fig. 24.1 Interaction potential between a 1- μm particle and a plane at different ionic strength of solution (I , M/L) (McDowell-Boyer et al. 1986). The surface potentials of the particle and the plane are equal to -30 mV

In solutions with the ionic strength of 0.5 M and more, diffusion layers contract to such a degree that van der Waals forces dominate all over the domain and no energy barrier exists to prevent colloidal particles from attaching to the mineral surface. As can be seen from Fig. 24.1, the distance between the particle and the surface is much less than the particle size.

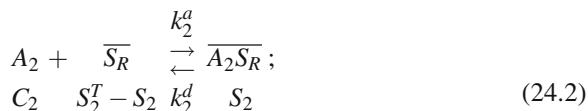
Colloids are known to be more stable in waters with sodium composition and less stable in waters with calcium composition, other conditions being the same (Kretzschmar et al. 1999; McCarthy and McKay 2004). Adsorption of natural organic matter (NOM) at the surface of inorganic colloids may positively or negatively influence aggregation processes. In most cases, higher concentrations of NOM tend to stabilize inorganic colloids. Moreover, an increase in organic matter content facilitates the mobilization of clayey colloids originally contained in rock and the dissolution of ferriferrous films on mineral grains, resulting in the appearance of a stable fraction of colloid oxides and iron hydroxides in pore solution. Overall, the stability of natural colloid systems is controlled by a number of physicochemical factors, whose role should be evaluated at the model level (Elimelech 1992; Grolimund and Borkovec 2001b).

24.2.2 Mobility and Accumulation of Colloids in the Porous Media

Colloids have the potential to move through groundwater systems with the same velocity or even faster than conservative (nonsorbing) solutes (Kim 1986; Ibaraki and Sudicky 1995; Kosakowsky 2004). This results from the relatively large size of the colloids, which tends to concentrate them in the middle of the pores where the groundwater velocity is larger than the bulk average velocity (Ibaraki and Sudicky 1995; Moridis et al. 2001). This is also due to the exclusion effect, manifesting itself in that colloids move along straighter trajectories relative to the solvent (water) and solute particle (prevailing migration paths appear). The molecules and ions that can penetrate into fine pores (fissure) and stagnant zones, into which colloid particles cannot enter because of their size, move slower. Thus, colloids reach the given point faster than the solute. However, experiments with suspensions (Ahfir et al. 2007) have shown that there exist critical values of Darcy velocity at which the exclusion effect manifests itself. The inverse picture can be observed at low Darcy velocities: the front of suspended particles moves slower than an inert tracer.

The filtration of colloid suspension is accompanied by accumulation of particles in porous (fractured) medium. This process in some cases may cause changes in the permeability of the aquifer material, and this phenomenon can be accounted for in mathematical transport models (McDowell-Boyer et al. 1986). In fractured media, the precipitation of particles on fracture walls enhances the storage capacity of the system with respect to dissolved pollutants.

Formally, the process of sorption (accumulation, attachment) of a colloid (A_2) onto solid matrix ($\overline{S_R}$) can be described by the following reaction:



here $\overline{S_R}$ symbolizes the binding sites attracting colloids; $\overline{A_2 S_R}$ is a colloid in the attached state; C_2 and S_2 are the colloid concentrations in the solution and on the solid matrix [ML^{-3}]; k_2^a and k_2^d are the rate coefficients for colloid attachment and release (units of [$\text{L}^3\text{M}^{-1}\text{T}^{-1}$] and [T^{-1}], respectively); S_2^T is the limit capacity for dispersed matter in the solid phase [ML^{-3}].

The rate of accumulation in a porous medium of colloids carried by water flow can be described by a kinetic equation of Langmuir type (van de Weerd et al. 1998):

$$P_2^S \equiv \frac{\partial S_2}{\partial t} = k_2^a C_2 (S_2^T - S_2) - k_2^d S_2. \quad (24.3)$$

Under equilibrium, we have $\partial S_2 / \partial t = 0$, whence we readily obtain the relationship $S_2 = f(C_2)$ (see below formula 24.15).

At the same time, experiments also revealed other mechanisms responsible for the precipitation of colloid particles. These mechanisms can be associated with the manifestation of gravitational effects, agglomeration of colloids, and their co-precipitation onto mineral surface along with other components. Therefore, the precipitation of colloids is considered in some papers in a generalized (“effective”) formulation as an irreversible process (McDowell-Boyer et al. 1986; Torok et al. 1990; Kretzschmar et al. 1997; Lührmann et al. 1998; Ibaraki and Sudicky 1995; Meier et al. 2003; Ahfir et al. 2007). It can be described by the first-order kinetic equation:

$$\frac{\partial S_2}{\partial t} = \lambda C_2, \quad \lambda = k_2^a S_2^T. \quad (24.4)$$

following from equation (24.3) applied to a linear domain $S_2 \ll S_2^T$ with $k_2^d = 0$.

Some authors suggest that the coefficient λ can be regarded as a linear function of the Darcy velocity q ($\lambda = \lambda_f q$), such that

$$\frac{\partial S_2}{\partial t} = \lambda_f q C_2, \quad (24.5)$$

where λ_f [L^{-1}] is the empirical filtration coefficient, depending on the size of colloidal particles, colloid composition, and the properties of porous medium.

An equation analogous to (24.5), for the filtration of a suspension solution in a single fracture has the form (Ibaraki and Sudicky 1995)

$$\frac{\partial \sigma}{\partial t} = \lambda_f u b C_2, \quad (24.6)$$

where σ is the mass of accumulated colloids per unit area of the fracture surface [ML^{-2}], u has the meaning of the real velocity of water flow in the fracture [LT^{-1}], b is the aperture of the fracture [L]. Analysis of some structure models allows us to proceed to evaluating λ_f (McDowell-Boyer et al. 1986; Meier et al. 2003).

Equations (24.5) and (24.6) describe an accumulation process, which is unidirectional and irreversible (the immobilized colloids cannot return into solution). A differential balance equation for colloids in such process can be written with the assumption that the migration of particles in porous medium is of piston type (without dispersion):

$$\phi \frac{\partial C_2}{\partial t} + q \frac{\partial C_2}{\partial x} = - \frac{\partial S_2}{\partial t}. \quad (24.7)$$

Its solution at $C_2|_{x=0} = C_{20}$ has the form

$$C_2 = C_{20} e^{-\lambda_f x}, \quad (24.8)$$

valid in the domain $qt/\phi \geq x$; when $qt/\phi < x$, $C = 0$. Colloid deposition onto a solid surface can also be modeled as a kinetic sorption process.

24.3 Sorption of Chemical Species onto Colloids (Under Batch Conditions)

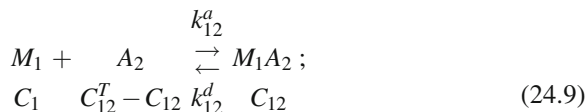
Colloids have high specific surface areas per unit mass (with values as high as $N \times 100 \text{ m}^2/\text{g}$) and high surface energy; thus they possess a high sorptive capacity for contaminants and are themselves readily able to sorb onto solid surfaces (Groffman and Meier 1993). The number of adsorption sites on colloids per unit mass is much higher than the analogous characteristic of the pore matrix. Accumulating matter on their surface, colloids can transport it over large distances.

Elements of physicochemical thermodynamics and kinetics can be used for the description of the adsorption interaction between colloidal particles and dissolved matter in the presence of porous matrix. Most widely used are models of physical adsorption, which allow one to account for the degree of reversibility of the process, which determines the ability of a colloidal particle to cast off the components it has adsorbed when the physicochemical state of the system changes.

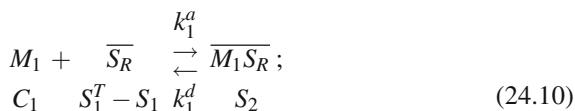
24.3.1 Basic Reactions

The adsorption equilibria in the “solution – colloids – solid phase” system are described in the general case by reactions that can be formalized in the following way (Lührmann et al. 1998; van de Weerd et al. 1998):

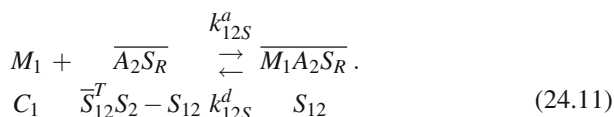
- (1) sorption of a dissolved component (contaminant), M_1 , onto a colloid, A_2 , forming a mobile colloidal complex, M_1A_2 :



- (2) sorption of a dissolved component (contaminant), M_1 , onto a solid (mineral) phase, $\overline{S_R}$, forming an immobile complex, $\overline{M_1S_R}$:



- (3) sorption of a dissolved component (contaminant), M_1 , onto attached colloids, $\overline{A_2S_R}$:



The following notations for concentrations were used: C_1 and C_2 are the contaminant and colloid concentrations in the liquid phase $[\text{ML}^{-3}]$; S_1 and S_2 are the contaminant and colloid concentration bound to the solid matrix $[\text{ML}^{-3}]$; C_{12} and S_{12} are the contaminant concentrations bound to mobile and immobile colloids $[\text{ML}^{-3}]$; C_{12}^T is the total number of sites available per mobile colloid, at that $C_{12}^T = \overline{C_{12}^T} C_2$ ($\overline{C_{12}^T}$ is the fraction of binding sites in mobile colloid $[-]$); S_1^T is the total number of sites available for contaminant sorption; S_2^T is the total number of sites available for colloid attachment; $\overline{S_{12}^T}$ is the total number of sites available per mobile colloid, at that $S_{12}^T = \overline{S_{12}^T} S_2$ ($\overline{S_{12}^T}$ is the fraction of binding sites per attached colloids available for contaminant sorption $[-]$); $k_1^{a/d}$ is the rate constant for sorption/desorption onto solid matrix (the dimension of sorption constant is $[\text{L}^3\text{M}^{-1}\text{T}^{-1}]$, the dimension of the desorption constant is $[\text{T}^{-1}]$), $k_{12}^{a/d}$ and $k_{12S}^{a/d}$ are the rate constants for sorption/desorption onto mobile and attached colloids (the dimension of the sorption constants is $[\text{L}^3\text{M}^{-1}\text{T}^{-1}]$, the dimension of the desorption constant is $[\text{T}^{-1}]$).

It is obvious that the equilibria (24.9)–(24.11) should be considered along with reaction (24.2) of precipitation (adsorption) of colloidal particles.

24.3.2 Governing Equations for Sorption Equilibrium

In accordance with the mass action law, reactions (24.2) and (24.9)–(24.11) correspond to the following isothermal equations relating the concentrations of a component in different phases:

$$C_{12} = \frac{K_{12} \bar{C}_{12}^T C_1 C_2}{1 + K_{12} C_1}, \quad K_{12} = \frac{k_{12}^a}{k_{12}^d}, \quad (24.12)$$

$$S_1 = \frac{K_1 S_1^T C_1}{1 + K_1 C_1}, \quad K_1 = \frac{k_1^a}{k_1^d}, \quad (24.13)$$

$$S_{12} = \frac{K_{12}^S \bar{S}_{12}^T S_2 C_1}{1 + K_{12}^S C_1}, \quad K_{12}^S = \frac{k_{12S}^a}{k_{12S}^d}, \quad (24.14)$$

$$S_2 = \frac{K_2 S_2^T C_2}{1 + K_2 C_2}, \quad K_2 = \frac{k_2^a}{k_2^d}. \quad (24.15)$$

The Eqs. 24.12–24.15 have the form of nonlinear Langmuir isotherms. In the linear domain, when the degree of saturation with matter of the immobile (rock matrix) and mobile (colloids) phases is small ($C_{12} < \bar{C}_{12}^T C_2$, $S_1 < S_1^T$, $S_{12} < \bar{S}_{12}^T S_2$, $S_2 < S_2^T$), the following relationships hold:

$$C_{12} = K_{12} \bar{C}_{12}^T C_1 C_2 = \bar{K}_{12} C_1 C_2, \quad (24.16)$$

$$S_1 = K_1 S_1^T C_1 = \bar{K}_1 C_1, \quad (24.17)$$

$$S_{12} = K_{12}^S \bar{S}_{12}^T S_2 C_1 = \bar{K}_{12}^S \bar{K}_2 C_1 C_2, \quad (24.18)$$

$$S_2 = K_2 S_2^T C_2 = \bar{K}_2 C_2; \quad (24.19)$$

here $\bar{K}_{12} = K_{12} \bar{C}_{12}^T$, $\bar{K}_1 = K_1 S_1^T$, $\bar{K}_{12}^S = K_{12}^S \bar{S}_{12}^T$, $\bar{K}_2 = K_2 S_2^T$.

Let us evaluate the character of solute distribution in the colloidal system, assuming adsorption of colloids on the mineral phase insignificant ($\bar{K}_2 = 0$). It can be readily seen that the process of component adsorption on colloids and the mineral matrix is governed by two “weight” coefficients of adsorption distribution: $K_d^c \equiv \bar{K}_{12}$ and $K_d \equiv \bar{K}_1 / \rho_b$ (ρ_b is rock density), which can be evaluated independently under the laboratory conditions. The coefficients K_d^c and K_d can be normalized relative to the effective area (A , cm²/g) of the two phases under consideration – colloidal A_c and rock A_R

$$K_d^c = K_a^c A_c \text{ and } K_d = K_a A_R, \quad (24.20)$$

where K_a is the coefficient of surface adsorption [cm].

When the coefficients K_d^c and K_a are equal, we have

$$K_d^c = F K_d, \quad (24.21)$$

where $F = A^c/A_R$ is the “adsorption reinforcing” coefficient (Vilks et al. 1998).

Studying the migration ability of some radionuclides (Am(III), Np(V), Pu(IV), Th(IV) and U(VI)), as applied to the hydrochemical conditions of aquifers within the proposed Yucca Mountain Nuclear Waste Repository site, made it possible to obtain a stable value of $F = 590$ (Contardi et al. 2001). Clearly, the introduction of “factor” F into the calculation scheme is justified only when the colloids originate from the processes of natural chemical weathering of the bed within which solutions are migrating.

We also give other data on the extent of sorption of components by colloids (Meier et al. 2003). The authors of the cited work give the following values of adsorption constants $K_d^c(\text{cm}^3\text{g}^{-1})$ for some metal ions on organic colloids typical of aquifers containing fresh waters with ionic strength $I = 2.6 \cdot 10^{-3} \text{ molL}^{-1}$, in the zone of potential impact of RW repository of Gorleben, Germany:

$$\begin{aligned} \text{Th}^{4+} &: (8.38\text{--}8.34) \cdot 10^6, \\ \text{Ac}^{3+} &: (1.80\text{--}1.93) \cdot 10^7, \\ \text{Pb}^{2+} &: (2.25\text{--}2.40) \cdot 10^5, \\ \text{UO}_2^{2+} &: (3.10\text{--}5.10) \cdot 10^5. \end{aligned}$$

Finally, the relationship (24.16), in particular, yields an expression for taking into account the degree of involvement of colloids in the retention of the substance in solution

$$\frac{C_{12}}{C_1^{\Xi}} = \frac{\bar{K}_{12} C_2}{1 + \bar{K}_{12} C_2} \equiv \frac{F K_d C_2}{1 + F K_d C_2}. \quad (24.22)$$

For example, with $F = 500$, $K_d = 1000 \text{ cm}^3/\text{g}$, and $C_2 = 1 \text{ mg/L} = 10^{-6} \text{ g/cm}^3$, we obtain $\tilde{N}_{12}/\tilde{N}_1^{\Xi} = 0.33$, i.e., 1/3 of components is retained in solution due to colloidal complexes.

24.3.3 Sorption Kinetics and Some Experimental Data

24.3.3.1 Basic Equations

The basic kinetic relationships follow from a formalized representation of exchange reactions (24.9)–(24.11):

(1) the kinetics of contaminant sorption onto mobile colloids:

$$P_{12} \equiv \frac{\partial C_{12}}{\partial t} = k_{12}^a C_1 \left(\bar{C}_{12}^T C_2 - C_{12} \right) - k_{12}^d C_{12}, \quad (24.23)$$

(2) the kinetics of contaminant sorption onto the solid matrix:

$$P_1^S \equiv \frac{\partial S_1}{\partial t} = k_1^a C_1 (S_1^T - S_1) - k_1^d S_1, \quad (24.24)$$

(3) the kinetics of contaminant sorption onto immobile colloids:

$$\frac{\partial S_{12}}{\partial t} = P_{12}^S + P^{SC}, \quad (24.25)$$

$$P_{12}^S = k_{12S}^a C_1 (\bar{S}_{12}^T S_2 - S_{12}) - k_{12S}^d S_{12}, \quad (24.25a)$$

P^{SC} in Eq. 24.25 is a term accounting for the mobilization or immobilization of contaminants bound to colloids due to interaction of colloids with solid matrix. This interaction term can be given by (Lührmann et al. 1998; van de Weerd et al. 1998)

$$P^{SC} = k_2^a C_{12} (S_2^T - S_2) - k_2^d S_{12}. \quad (24.25b)$$

The equation of colloid precipitation kinetics $P_2^S = \partial S_2 / \partial t$, supplementing the system of Eqs. 24.23–24.25, has the form (24.3).

24.3.3.2 Some Experimental Data Obtained for Liquid Colloid Systems Containing Radionuclides

The kinetics of adsorption–desorption processes is less known than the equilibrium state of disperse systems containing some adsorbable element. Some publications mention that the components that form surface complexes with colloids (e.g., transition metals, actinides) show slow adsorption kinetics. In many cases, adsorption can be interpreted as an irreversible process (at the time scale comparable with the residence time of pollutant in the aquifer).

Thus, Vilks with co-workers (1993), who studied the distribution in groundwater of colloid-associated actinides (a part of the Cigar Lake uranium deposit), were among the first to come to the conclusion that the desorption of radionuclides can be very slow, allowing them to penetrate with particles-carriers into the parts of the aquifer where almost no radionuclides occur in dissolved form.

Low kinetic characteristics of desorption release of Pu(V) from colloid particles, represented by montmorillonite, smectite, silicon earth, and hematite, were recorded in laboratory experiments (Painter et al. 2002); a dual-site kinetic model was used to process their results. In this work, it is also noted that the lack of data on desorption kinetics makes the forecasts of radionuclides' migration in colloidal form very uncertain.

Thus, Penrose with co-workers (1990), in their experiments with plutonium, found no signs of its desorption during 2-day desorption stage, while parallel experiments with americium showed fast desorption kinetics. Similar experiments with radioactive pollution of soils, carried out by Bunzl with co-workers (1995), revealed the same trend.

Table 24.1 Percent concentration of radionuclides adsorbed by colloids of different size (Tanaka et al. 2003)

Particle size, nm	²⁴¹ Am	²³⁷ Np
>450	44.8	10.1
100–450	27.4	1.6
50–100	0.0	0.0
20–50	0.2	0.0
6–20	0.0	0.0
2–6	25.5	7.8
<2	2.1	80.5

Conversely, studies of ²⁴¹Am(III) migration (with parallel experiments with ²³⁷Np(IV)) in a column filled by loess material have led to the conclusion that americium adsorption on colloidal particles is irreversible (Tanaka et al. 2003). This conclusion was based on the obtained distribution of americium over the length of the flow column; this distribution demonstrated its high mobility (with the distribution coefficient, K_d , found in preliminary static experiments to be about 10,000 cm³/g). At the same time, the relatively low K_d of neptunium (on the average, about 300 cm³/g) resulted in the adsorption of the entire injected amount of this radionuclide near the entry of the column. It is also worth noting that the solution prepared from the pore liquid of the examined sample was used first to study the size distribution of colloid particles by filtering through a series of membranes (Table 24.1). If we assume that only ionic forms of radionuclides persist in solution after filtering through a membrane with pore diameter <2 nm, the above data imply the prevalence of colloidal form of americium migration; the formation of colloidal associations for neptunium is not as typical as that.

The effect of adsorption and desorption kinetics of ²⁴¹Am(III), transported by organic colloids ($C_{Am} = 8.7 \cdot 10^{-6}$ mol/L, solution ionic strength of 0.044 M, pH 7.6, NOM concentration of 80 mg/L), on the concentration distributions (Kim et al. 1994) was evaluated in the process of model interpretation of an experiment in a flow column with rock material taken at the Gorleben waste disposal site (van de Weerd and Leijnse 1997; van de Weerd 2000). A satisfactory agreement between experimental and model results was observed at relatively low desorption coefficient $k_{12}^d = 2.58 \cdot 10^{-2} \text{ h}^{-1}$ (with $k_{12}^a = 1.36 \cdot 10^{+4} \text{ L}/(\text{mol h})$ – see Sect. 24.3.1). Attempts to interpret data within the framework of equilibrium model ($K_{12} = k_{12}^a/k_{12}^d = 5.18 \cdot 10^{+5} \text{ L}/\text{mol}$ – see Sects. 24.3.1, 24.3.2 and 24.3.3.1) proved a failure. A correct description of tailing effects required the incorporation in the model of adsorption and desorption kinetics, characterizing the interaction between colloidal particles and the mineral matrix.

A very low kinetic rate of plutonium desorption (Pu(V) in the ionic form and Pu(IV) in the form of true colloids) was also recorded in experiments with colloids represented by iron oxides – hematite and goethite (Lu et al. 1998a, b). It was concluded that the difference between the adsorption and desorption constant established in experiments with plutonium can determine the higher rate of ²³⁹Pu migration in groundwater.

Batch and column (dynamic) laboratory experiments were carried out to study the behavior of colloidal forms of plutonium migration (Pu(V) and Pu(IV)) under the conditions of Nevada Test Site, USA (Reimus et al. 2001). Montmorillonite and silicon earth colloids were used as vehicles for Pu(V), and clinoptilolite, for Pu(IV). After the adsorption stage examined in static experiments, in which adsorption kinetics was measured during about 3 weeks, Pu-colloid suspension was injected into a fracture created in a laboratory sample (a dynamic experiment). The desorption process was examined independently. It was established, in particular, that the ability of colloids to transport Pu is characterized by the series clinoptilolite > montmorillonite > silicon earth. Moreover, it was found that Pu adsorbed on clinoptilolite was not desorbed either in static or in dynamic experiments.

Schäfer with co-workers (Schäfer et al. 2001, 2002) note that the interaction of actinides with metastable colloidal ferrohydrate during the recrystallization of the latter into stable hematite and (or) goethite is an irreversible reaction.

Of particular interest is the experimental estimation of the constants of formation (λ_1) and decay (λ_2) of M_1A_2 particles. Thus, the values of $\lambda_1 = 720 \text{ d}^{-1}$ and $\lambda_2 = 2.4 \text{ d}^{-1}$ found in experiments (Torok et al. 1990) show a sufficient strictness of the equilibrium model (24.9), designed for studies (forecasts) at a field scale.

In other experiments (Saiers and Hornberger 1996), it was shown that the presence of a clay mineral, kaolinite, in the solution of colloids (up to 200 mg/L) doubles the migration capacity of ^{137}Cs . The same authors in another work (Saiers and Hornberger 1999) estimated the effect of the ionic strength of solution on the mobility of kaolinite colloids: it was established that the mobility of colloids and their capacity to adsorb ^{137}Cs decline with increasing ionic strength.

The results of experiments with membrane filtration of groundwater polluted by ^{210}Po and ^{210}Pb (Lehto et al. 1999) showed that only 1–2% of these radionuclides occur in dissolved form. The size of colloidal particles that adsorb radionuclides is different in different water samples. Thus, in one sample, about 80% of ^{210}Pb was contained on colloids with a size of 450 nm, while in other one, 50% of ^{210}Po was adsorbed on colloids with a size varying from 100 to 450 nm.

It can be seen that of greatest interest for researchers is the evaluation of the migration capacity of plutonium, which is among actinides that are the greatest threat to human health. Plutonium may simultaneously occur in solutions in several redox states (forms), including true colloids; this fact makes it difficult to interpret the behavior of Pu in hydrogeological systems (see Sect. 27.3.1). To study the migration capacity (controlled, in particular, by adsorption) of individual forms of plutonium, it is of use to utilize stable (in terms of the invariant character of behavior in systems with different redox potential) cations–analogues of this actinide. We mean the analogues, whose behavior is exactly the same as that of plutonium in different states. Examples of such analogues can be (Choppin 1999): Eu(III) and Am(III) for Pu(III), Th(IV) for Pu(IV), Np(V)O^+_2 for Pu(V)O^+_2 and U(VI)^{2+}_2 for Pu(VI)^{2+}_2 .

24.4 Subsurface Behavior of Actinides at Existing and Proposed RW Disposal Sites

In the recent decade, the progress in development of analytical techniques, accompanying the radioecological monitoring of groundwater quality in areas with radioactive pollution, made it possible to establish numerous facts suggesting the possible transport of radionuclides in small concentrations over large distances from pollution sources. These facts refer primarily to the migration of actinides, which have been long considered (because of their low solubility in water and high adsorption by sediments and rocks) as components with low mobility in the subsurface hydrosphere. This circumstance, associated with the formation of mobile actinide–colloid systems, stimulated diverse studies not only at sites that have already experienced radiation impact, but also in the areas of possible construction of repositories for radioactive waste with different degrees of toxicity. The appropriate programs, whose implementation requires large financial expenses, are of higher priority in many national research laboratories.

24.4.1 Sites Where Pu and Some Other Actinides Have Been Detected in the Environment

At the *Nevada Test Site*, a considerable amount of plutonium has been accumulated in rocks because of underground nuclear weapon tests. Preliminary modeling of plutonium migration process yielded very optimistic forecasts, implying very high degree of localization of the radionuclide around the explosion site. However, more recent studies (Kersting et al. 1999), including, in particular, examining the isotope ratio $^{240}\text{Pu}/^{239}\text{Pu}$, demonstrate active migration of plutonium in colloidal form (illite, smectite, zeolite), resulting in the appearance of this radionuclide in checkpoints 1.3 km from the pollution sources about 45 years after the beginning of the test.

Weapon-grade plutonium production at *Hanford Site* plants have resulted in the formation of large amounts of radioactive and mixed wastes. Their considerable portion (about 350 thousand m^3) is stored in subsurface tanks as low- and high-activity liquid wastes (Hakem et al. 1999). Detailed studies aimed to detect plutonium pollution in groundwater (Dai et al. 2005) were carried out in 1999 at “100-K” site, Columbia River valley, where nine nuclear reactors are situated. Of greatest environmental hazard are two basins containing radioactive water and incorporated in a system of radioactive fuel storage. The inflow of pollution into the rocks underlying the basins and into the aquifer beneath them was due to solution leakages from the basins.

Water sampling from observational well network showed plutonium isotope concentrations in groundwater to be relatively low: 10^{-6} – 10^{-8} pCi/L $\approx 10^4$ – 10^6 at/L; in this case, only 7–29% of plutonium is associated with the colloidal fraction.

Therefore, the potential for colloidal transport in groundwater is sometimes a source of uncertainty with respect to future Pu migration at Hanford site (Cantrell and Riley 2008).

Examining the $^{240}\text{Pu}/^{239}\text{Pu}$ isotope ratio was an important element of the study. The obtained values of $^{240}\text{Pu}/^{239}\text{Pu}$ appreciably differ from the value $^{240}\text{Pu}/^{239}\text{Pu} \approx 0.18$, typical of global atmospheric fallouts associated with nuclear weapon tests. Thus, the authors came to the conclusion that the sources of plutonium in groundwater are radioactive materials associated with production processes at the site and having nothing in common with global fallouts. On the other hand, the plutonium pollution of the Columbia River is exclusively due to the atmospheric plutonium.

Another industrial plant, involved in the production of weapon-grade nuclear components (such as ^3H , ^{239}Pu), as well as ^{238}Pu and other transplutonium radionuclides for medical and research purposes, is the *Savannah River Site* complex, situated in the western part of South Carolina. Radioactive wastes, containing in particular ^{239}Pu ($^{240}\text{Pu}/^{239}\text{Pu} = 0.062$), have been discharged into surface basins; the total activity of the discharged ^{239}Pu was 209 GBq (1 GBq = 10^9 Bq). The radioactive wastes, represented by acid solutions high in nitrate salts, partially entered groundwater because of leaks from the basins.

Studies carried out at some site (Dai et al. 2002) have shown that the oxidation degree of ^{239}Pu in groundwater is higher (Pu(V) and Pu(VI)) than at the Hanford Site, and only a small part of plutonium (less than 4%) is associated with colloidal fraction. The higher values of $^{240}\text{Pu}/^{239}\text{Pu}$ ratio at some sites are due to the decay of the transplutonium element ^{244}Cm , yielding a daughter product, ^{240}Pu . Overall, the migration capacity of plutonium in groundwater is relatively low.

Rocky Flats Site (24 km from Denver, Colorado, USA) is the territory of the former plant for production of nuclear and conventional weapons (it was functioning from 1952 to 1989). Since 1995, a rehabilitation program has been implemented in the territory. The storage of low-radioactivity waste and wind-induced dispersion of radioactive materials caused soil pollution by actinides (Pu, Am, and U are the major representatives of radionuclides). According to the data of initial studies, $^{239-240}\text{Pu}$ concentration in soils was $1.85-5.4 \cdot 10^4$ Bq/kg; ^{241}Am concentrations are an order of magnitude less than that (Krey 1976; Litaor 1995). More recent studies (Clark et al. 2006), which made it possible to compile a detailed map of plutonium concentration in near-surface deposits, confirmed the pollution level identified before. More than 90% of Pu is contained in the top 10–12-cm soil layer. The admissible level of soil pollution was estimated at $1.85 \cdot 10^3$ Bq/kg. According to different estimates, not more than 1% of total radionuclide content reaches groundwater.

In this area, colloidal transport of plutonium and americium determines the main hazard of surface water pollution (actinide concentration in it varies within $10^{-15}-10^{-13}$ Ci/L), caused by hillside erosion (Cantrell and Riley 2008). The main role in the near-surface actinide transport belongs to colloids of organic origin, which have a negative charge and a molecular mass reaching 10,000–15,000. Studies of the size distribution of colloid particles were based on ultrafiltration, which made it possible to determine the prevailing (about 60%) size of particles within the range from 100 to 500 nm.

Studies carried out in a groundwater pollution site near *Lake Karachai* (Chap. 15) showed (Novikov et al. 1998; Ivanov et al. 2005) that some actinides (primarily, $^{239,240}\text{Pu}$ and ^{241}Am) in anthropogenic solutions also form stable complexes associated with mineral particles. Their relative concentration exceeds 50% of the total concentration of radionuclides of this type within the groundwater pollution zone. The share of plutonium in the colloidal state increases considerably in groundwater where higher concentrations of dissolved organic matter are recorded (Ivanov 2004).

It was found that 70–90% of plutonium (IV) is associated with colloidal particles whose size varies from 1 to 15 nm (Novikov et al. 2006); according to other data, 95% of actinide elements are concentrated in fine (<5–50 nm) fractions. These particles are mostly represented by amorphous oxides and hydroxides of iron. The ratio of plutonium concentration on colloids to the concentration of plutonium in ionic form varies from about 2.2 (near pollution source) to more than five (at a distance more than 2.15 km from pollution source downstream groundwater flow). Plutonium concentrations in wells in the zone of potential groundwater discharge in Myshelyak River valley vary from hundredths to tenths fractions to 3 Bq/L. Plutonium concentration in pollution source is about 1000 Bq/L. Thus, a significant level of groundwater pollution by plutonium was recorded at a distance of about 4 km from Karachai Lake about 55 years after the beginning of radioactive waste discharge into the lake.

The transport behavior of Pu at several sites within the DOE complex (including sites considered above), as well as at one U.S. commercial site and Mayak site (Chap. 15) was also reviewed in a document by Cantrell and Riley (2008). This review suggests that colloid-facilitated transport has generally been overstated in performed site assessments.

24.4.2 Designed and Engineered Repositories for RW Disposal

According to preliminary estimates of the environmental impact of the proposed Yucca Mountain Nuclear Waste Repository site, Nevada, USA, the major hazard to groundwater quality will be the migration of actinides associated with anthropogenic (waste-form, the size of 6–450 nm) and natural (clayey particles, silicon earth, and zeolites with the concentration of $1.05 \cdot 10^9$ – $2.72 \cdot 10^{13}$ particles/L) colloids (Lu et al. 1998a; UZ Colloid Transport Model 2000; Contardi et al. 2001) with the anthropogenic colloids assumed to be predominant. Batch laboratory experiments with adsorption and desorption of Pu(IV) and Pu(V) showed the desorption kinetic constant to be on the average 4–5 orders of magnitude less than the respective characteristic of adsorption process (N and $N \cdot 10^{-5} \text{ s}^{-1}$, respectively).

A special study was devoted to the analysis of the sensitivity of the process of groundwater radioactive pollution in the given area to the transport of radionuclides Am(III), Th(IV), Pu(V), U(VI), and Np(V) by natural colloids

(Contardi et al. 2001). The analysis was based on data on the coefficients of surface adsorption distribution K_d (19.1a), obtained by modeling thermodynamic equilibrium in the rock–groundwater system with an “enhancement” coefficient $F = 590$ (24.21). Calculations showed that the colloid transport of the most actively adsorbed Am and Th is the greatest groundwater pollution hazard, because these radionuclides are best retained by colloids. The process of radiocolloids’ formation has practically no effect on the transport of U and Np. In these estimates, adsorption was assumed reversible.

Experimental laboratory studies (Schäfer et al. 2002) reproducing the conditions of *Grimsel Test Site*, Switzerland, in fractured granites (Central Aar Massif), showed that the formation of a contact between bentonite, used to construct engineering barriers, and water-bearing rocks leads to the formation of smectite colloids (up to 17.5 mg/L). These colloids, which are stable in the groundwater of the area, are able to transport actinides, and this effect should be taken into account in the safety estimates of RW repository construction.

Studies carried out under field conditions consisted in the injection through a well into the fractured zone of a tracer “cocktail” in two variants (Nagra Bulletin 2002; Delos et al. 2002): (1) a colloid-free solution, containing ^{243}Am , ^{237}Pu , ^{238}Pu , ^{238}U , ^{85}Sr , ^{232}Th , and (2) a solution containing bentonite colloids (20 mg/L) and radionuclides ^{241}Am , ^{237}Np , ^{238}Pu , ^{244}Pu , ^{233}U , ^{99}Tc , ^{137}Cs , ^{85}Sr , ^{232}Th . The breakthrough curves obtained in the experiment demonstrate a considerable effect of colloids on radionuclide transport, in particular, the presence in solution of bentonite colloids with small diameter accelerates radionuclide transport.

The importance of studying radionuclide migration in colloid-bound form under the conditions typical of the area under consideration was also confirmed by laboratory experiments with Cs, U(VI), and Tc(IV) isotopes (Missana et al. 2001); experiments with Tc(VII) and Se(IV) showed no appreciable adsorption of these radionuclides on bentonite.

Typical representatives of the colloid fraction of groundwater in the formation chosen for the construction of a repository in Germany, *Gorleben Site*, are metastable, dyscrystallized ferrohydrates (2LFh); they are also present in the form of films on minerals in solid phase in the porous matrix. Studies of Schäfer et al. (2002) showed the stability of colloidal fraction to be determined by the concentration of dissolved organic substances (DOC) in water: a rapid coagulation of 2LFh-colloids was recorded in waters with lower concentration of DOC (0.9–5.0 mg/L), while the system was stable at higher DOC concentration (22.6–81.6 mg/L). The concentration of colloids was 1.85–5.6 mg/L.

The stabilization of colloid system plays an important role in the acceleration of radionuclide transport as can be seen from the data of dynamic experiments (Schäfer et al. 2002) with ^{241}Am (III): the use in experiments of groundwater enriched with organic matter have resulted in a fivefold increase in the migration velocity of americium in 2LFh-colloidal and organometallic (complex) forms.

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Chapter 25

Experimental Study of Radionuclide Interaction with Colloids with Respect to Tomsk-7 Deep-Well RW Disposal in a Geological Formation

Colloid-facilitated transport is still an issue in a division of contaminant hydrology related to radioactive solution migration in the subsurface environment. Sophisticated phenomenological transport models are available, but progress is required to fully understand mechanisms and parameters. This study focuses on this experimental direction.

Both synthesized radioactive solutions, containing clay particles, and samples of formation water containing natural colloids were used for studying radionuclide sorption onto colloids. To study radionuclide distributions on colloid particles of different genesis and size, the researchers used ultrafiltration as a technique for separating colloid fractions in solution (Zakharova et al. 2007). The experiments were aimed at the study of radionuclide behavior at the Tomsk-7 site, which includes two deep recharge well clusters (RWC-18 and RWC-18 a) for disposal of liquid LLW and ILW (Fig. 25.1) in a geological formation (see Sects. 3.4.4 and 23.1).

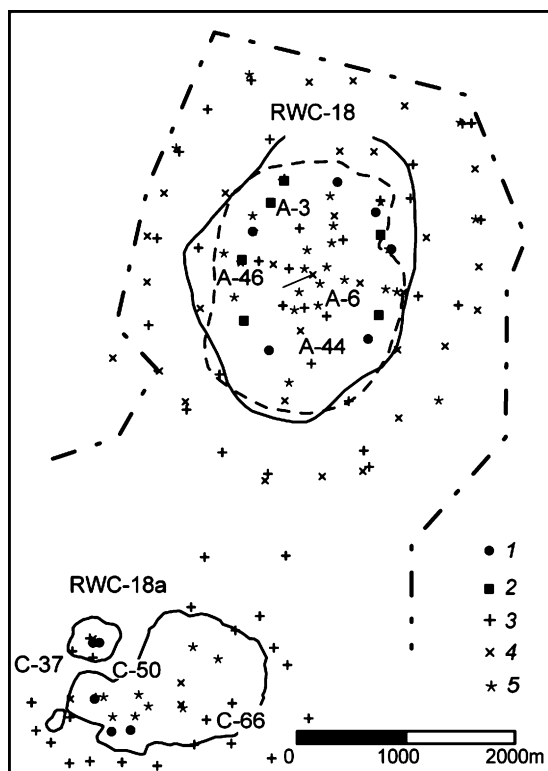
The previously discussed laboratory data illustrate that radionuclide retention capacity of the aquifer material depends on the chemical behaviors of the principal components and can be estimated as relatively high. Until recently, however, the role of colloidal transport of these elements was not clear. This section presents the results of studying synthesized solutions containing clay particles and groundwater samples aimed to assess the ability of some actinides and fission radionuclides to form intrinsic (true) colloids and pseudocolloids.

25.1 A Study of Sorption of Plutonium on Colloids in Ultrafiltration Experiments with Synthesized Solutions

25.1.1 Experimental Setup

Sorption of plutonium Pu(IV) on clay particles (with a size <0.001 mm) from model solutions was studied. The clay fraction was isolated from core-samples taken from one of the wells, penetrating the host-aquifer of the RW disposal site (Fig. 25.1).

Fig. 25.1 Well location within Tomsk-7 RW disposal site. 1 and 2 are the recharge wells penetrating the II and III aquifers; 3, 4 and 5 are the observation wells penetrating the II, III and IV aquifers (numbers belong to the wells which were used for colloid sampling). *Solid lines* delineate zones occupied by radioactive solutions in the II aquifer; *dashed lines* are the same for the III aquifer (2004). The *dot-dash line* marks the boundary of the waste disposal site (restricted zone)



The mineralogical composition and the concentration of clay minerals were determined by X-ray phase analysis. The clay fraction is mostly represented by kaolinite and chlorites (87.1–91.7%); illite (6.4–9.3%) and montmorillonite (1.8–2.2%) occur in lesser amounts. Membrane ultrafiltration of solutions, containing only clay particles, was carried out before the experiments. The particle size distribution of the colloid preparations was evaluated by sequential filtration through etched polycarbonate nuclear membranes with the following pore sizes: 400, 200 and 100 nm.

The amounts of particles with different sizes retained by membranes with different pore diameters (Φ_i) was determined by weighing on analytical balance (OHAUS) with an accuracy of 0.0001 g (Table 25.1). This made it possible to evaluate clay particle concentrations (C'_i , $i = 2, 3, \dots, N + 1$, see below), referring to fractions of particles with different sizes (Table 25.3). In particular, the obtained values show that the concentration of clay particles with a size more than 400 nm is 65–70%.

Model solutions contain sodium nitrate (50 mg/L), represent two pH ranges (6.4–6.9 and 4.6–5.0), and have the initial plutonium concentrations of, Bq/L: 10^6 , 10^5 , and 10^4 . The amount of sodium nitrate corresponds to its concentration in the slightly contaminated water. The procedure consisted of sequential filtration of radioactive solutions through 400, 200, 100, and 5-nm membranes.

Table 25.1 Ultrafiltration of nm-clay particle suspension (Pu-free system)

Pore size of nuclear filter, Φ_i , nm	Initial content of clay fraction in 100 ml of solution, mg			
	1.5		3.0	
	Content on the filter surface			
	mg	%	mg	%
400	0.969	64.6	2.13	71.0
200	0.331	22.1	0.735	24.5
100	0.196	13.1	0.147	4.9

Table 25.2 Results of ultrafiltration of NO₃ solutions containing Pu

i^a	Φ_i , nm	C'_i , mgL $^{-1}$	pH = 6.4-6.9		pH = 4.6-5.0	
			${}^T C_1^i$	${}^T C_1^i$	${}^T C_1^i$	${}^T C_1^i$
$C \cdot 10^{-6}$ BqL $^{-1}$						
		9.69	1.000	1.000	1.000	1.00
4	400	3.31	0.624	0.298	0.652	0.41
3	200	1.96	0.479	0.212	0.607	0.37
2	100	<0.1	0.453	0.185	0.583	0.17
1	5		0.196	0.090	0.163	0.02
$C \cdot 10^{-5}$ BqL $^{-1}$						
		9.69	1.000	1.000	1.000	1.00
4	400	3.31	0.399	0.162	0.633	0.19
3	200	1.96	0.367	0.127	0.501	0.09
2	100	<0.1	0.333	0.102	0.471	0.07
1	5		0.160	0.056	0.197	0.04
$C \cdot 10^{-4}$ BqL $^{-1}$						
		9.69	1.000	1.000	1.000	1.00
4	400	3.31	0.626	0.167	0.529	0.49
3	200	1.96	0.547	0.128	0.382	0.29
2	100	<0.1	0.507	0.111	0.236	0.25
1	5		0.187	0.030	0.181	0.16

^a The number of the membrane

The ultrafiltration of solutions containing no clay component showed a decrease in the total activity of Pu (${}^T C_1^i$) after each i -th ultrafiltration step (Table 25.2), suggesting the presence of intrinsic Pu colloids in the solutions, where these colloids are also represented by several fractions (Fig. 25.2). The experiments revealed some regularities common for all examined concentrations: the amount of coarse particles (>400 nm) averages $40 \pm 5\%$, while that of fine particles (<5 nm) is $15 \pm 5\%$. However, no effect of pH on the size distribution of plutonium particles was recorded in the examined pH interval.

During ultrafiltration of radioactive solutions containing 15 and 30 mg/L of clay particles (<0.001 mm), it was established that Pu concentrations in the samples after filtration ${}^T C_1^i$ (Table 25.2, Fig. 25.2) differs from the values ${}^T C_1^i$, determined at the

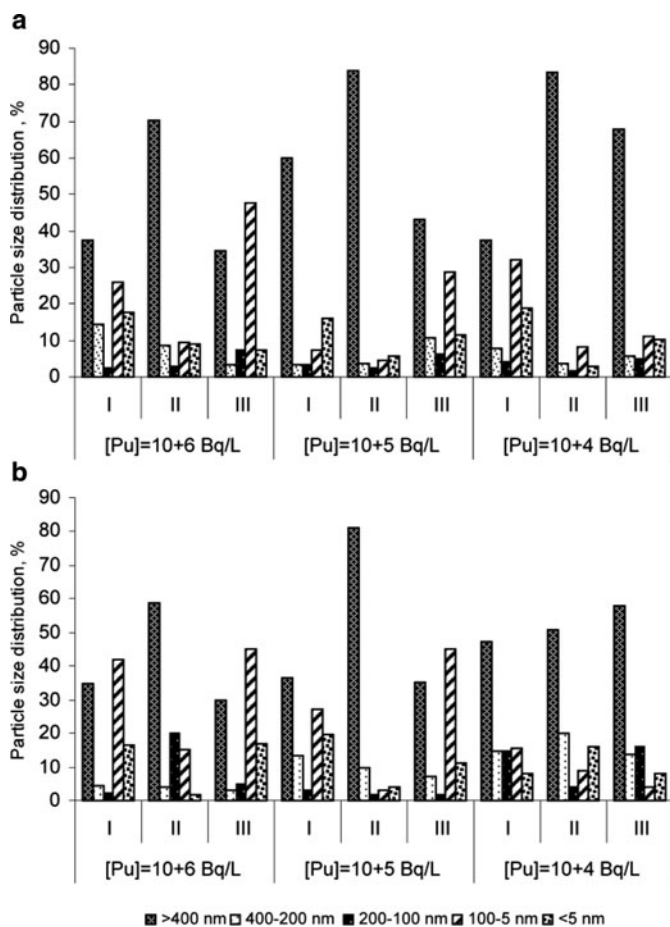


Fig. 25.2 Pu distribution in liquid phase after ultrafiltration of synthesized sodium nitrate solutions. (a) pH 6.4–6.9; (b) pH 4.6–5.0. (I) No clay particles; (II, III) clay particle content: (II) 15 mg/L, (III) 30 mg/L

same steps in experiments with solutions containing no clay particles. This suggests plutonium sorption on such particles. In systems containing 15 mg/L of clay fraction, the amount of *Pu-carrying particles* with a size of more than 400 nm increases appreciably, while the concentration of such particles with a size of less than 100 nm decreases. Such tendency was observed for all examined Pu concentrations and for both pH intervals. We can suppose that, since the concentration of clay particles with a characteristic size of less than 100 nm is insignificant (see Table 25.2), the entire plutonium with particle size below 100 nm occurs in the form of its own colloids.

25.1.2 Interpretation of Experimental Results

25.1.2.1 Problem Formulation

As it was noted in the methodological section, the experimental data suggest the presence of colloidal plutonium in the initial model solutions. Therefore during successive ultrafiltration, the membranes retain not only clay particles that have adsorbed plutonium but also the intrinsic colloids of this actinide (and sometimes much more the latter than the former). Thus, the experiments study a colloid system containing several fractions, differing in the mean size of their particles and represented by both clayey particles (mineral colloids) and Pu colloidal forms (intrinsic colloids).

The number of the examined fractions of pseudocolloids carrying Pu (N) and intrinsic Pu-colloids (M) is determined by the set of membranes available in the laboratory. Since the filtration through membranes yields the separation of both mineral and intrinsic colloids into the same number of fractions, we have $N = M$; however, we will still use double indexation for convenience sake. Each fraction can be characterized by the average particle size (Φ_i^{av}), representing it. This size lies within the range $\Phi_i < \Phi_i^{\text{av}} < \Phi_{i+1}$, where Φ_i is the pore diameter of the i -th membrane.

The presence of colloidal particles of different genesis significantly complicates the interpretation of experiments, whose principal aim is to evaluate the partial constants (coefficients) of sorption distribution of Pu on clay particles belonging to each fraction.

By partial distribution coefficients $\bar{K}_{1i}$ we mean the coefficients of reaction of chemical sorption equilibrium, which determine the sorption of Pu ions ($M_1 \equiv \text{Pu(IV)}$) by the i -th fraction of clay particles (A_i):



such that the concentration of plutonium adsorbed by this fraction becomes

$$C_{1i} = \bar{K}_{1i} C_1 C_i; \quad (25.1a)$$

here C_1 is the concentration of Pu ions; C_i is the concentration of clayey particles belonging to the i -th size fraction.

The solution contains intrinsic Pu colloids, which also can be adsorbed on clayey particles, the fact that complicates the interpretation scheme of experiments. The appropriate chemical reactions yield “colloidal–mineral” complexes C_{ji} , where $i = 2, 3 \dots N + 1$, $j = N + 2, N + 3, \dots, N + M + 1$. By analogy with the

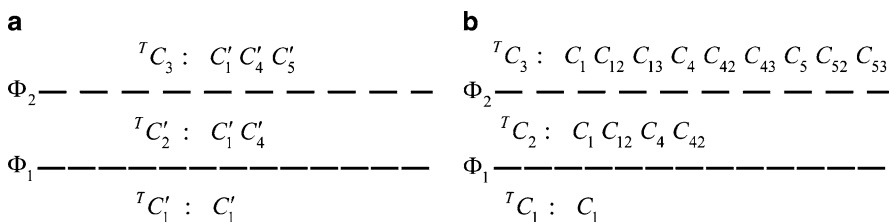


Fig. 25.3 Specification of Pu concentrations in different forms during two-step ultrafiltration. (a) Filtration of the initial (without clay particles) solution; (b) filtration of solution containing two mineral fractions. Strokes conventionally mark membranes, Φ_2 , Φ_1

above-considered process (25.1), the complex-formation reactions involving mineral and intrinsic colloids can be written as



where

$$C_{ji} = \bar{K}_{ji} C_j C_i. \quad (25.2a)$$

Thus, the equilibrium process is characterized by the distribution coefficients $\bar{K}_{ji}$.

Consider the construction of models that enable one to evaluate the partial coefficients of sorption distribution by using the results of experiments with (multi-step ultrafiltration). The simplest variant of fragmentation of the system with the identification (specification) in the system of two fractions, i.e., pseudocolloids and intrinsic colloids, is shown in Fig. 25.3.

25.1.2.2 System Specification and Model Development

Assume that clay (mineral) material was dispersed in the solution with total content of Pu, ${}^T C_1^{N+1} = {}^T C_1^{N+1}$ (comments to notations will be given later). Weighted concentrations of the mineral fractions with different average particle sizes ($\Phi_2^{\text{av}} < \Phi_3^{\text{av}}, \dots, < \dots, \Phi_{N+1}^{\text{av}}$) are $C'_2, C'_3, \dots, C'_{N+1}$ (N is the total number of fractions). The concentration of the ionic Pu form in the initial solution is C'_1 . Upon their introduction into the initial solution, clay particles sorb ionic and colloidal plutonium forms. Therefore, the concentration of ionic forms and Pu-free mineral particles in solution decreases to the values of C_1 and $C_2, C_3, \dots, C_{N+1}$.

The concentration of intrinsic colloids of Pu in the initial (free of clay particles) solution is $C'_{N+2}, C'_{N+3}, \dots, C'_{N+M+1}$, and that in the second solution, containing clayey particles, is $C_{N+2}, C_{N+3}, \dots, C_{N+M+1}$. The interaction between clay particles with Pu ions (25.1) and intrinsic colloids (25.2) yields complexes $C_{12}, C_{13}, \dots, C_{1(N+1)}$ and $C_{(N+2)2}, C_{(N+3)2}, \dots, C_{(N+M+1)2}, \dots, C_{(N+2)3}, C_{(N+3)3}, \dots, C_{(N+M+1)(N+1)}$.

Suppose (Fig. 25.3) that each membrane used to filter solutions at the first, second, and subsequent steps can fractionate colloids, separating Pu adsorbed by each fraction of clay particles and the fractions of intrinsic Pu colloids. The last membrane passes only “ionic” Pu. Since two experiments are carried out simultaneously (one involving the original solution and the other involving the same solution with addition of clayey fractions), we can compare the total Pu concentrations measured at each filtration step. Denote these concentrations as ${}^T C_1^N, {}^T C_1^{N-1}, \dots, {}^T C_1^1 = C_1'$ and ${}^T C_1^N, {}^T C_1^{N-1}, \dots, {}^T C_1^1 = C_1$ respectively. Before the ultrafiltration, we have ${}^T C_1^{N+1} = {}^T C_1^{N+1}$.

Write the basic balance equations:

for the ionic Pu form

$$C_1' = C_1 + \sum_{i=2}^{N+1} C_{1i}; \quad (25.3)$$

for the intrinsic Pu colloids

$$\begin{aligned} C_{N+2}' &= C_{N+2} + \sum_{i=2}^{N+1} C_{(N+2)i}, \\ C_{N+3}' &= C_{N+3} + \sum_{i=2}^{N+1} C_{(N+3)i}, \\ &\dots\dots\dots, \\ C_{N+M+1}' &= C_{N+M+1} + \sum_{i=2}^{N+1} C_{(N+M+1)i}; \end{aligned} \quad (25.4)$$

for mineral colloids

$$\begin{aligned} C_2' &= C_2 + C_{12} + \sum_{j=N+2}^{2N+1} C_{j2}, \\ C_3' &= C_3 + C_{13} + \sum_{j=N+2}^{2N+1} C_{j3}, \\ &\dots\dots\dots, \\ C_{N+1}' &= C_{N+1} + C_{1(N+1)} + \sum_{j=N+2}^{2N+1} C_{j(N+1)}. \end{aligned} \quad (25.5)$$

Adding the left and right parts of equations in the systems (25.3) and (25.4), we obtain a generalized expression for the total concentration in the initial (before filtration through membranes) solution containing clayey particles

$${}^T C_1^{N+1} = C_1 + \sum_{i=2}^{N+1} C_{1i} + \sum_{i=N+2}^{N+M+1} C_i + \sum_{j=N+2}^{N+M+1} \sum_{i=2}^{N+1} C_{ji}. \quad (25.6)$$

From this equation, by successive exclusion method, we obtain additional equations of Pu balance in solutions after passing several (N) membrane filtration stages:

$$\begin{aligned}
 {}^T C_1^N &= C_1 + \sum_{i=2}^N C_{1i} + \sum_{i=N+2}^{N+M} C_i + \sum_{j=N+2}^{N+M} \sum_{i=2}^N C_{ji}, \\
 {}^T C_1^{N-1} &= C_1 + \sum_{i=2}^{N-1} C_{1i} + \sum_{i=N+2}^{N+M-1} C_i + \sum_{j=N+2}^{N+M-1} \sum_{i=2}^{N-1} C_{ji}, \\
 &\dots\dots\dots, \\
 {}^T C_1^1 &= C_1.
 \end{aligned} \tag{25.7}$$

The concentrations C_{1i} and C_{ji} are related with the partial coefficients of sorption distribution $\bar{K}_{1i}$ and $\bar{K}_{ji}$ by formulas (25.1a) and (25.2a). Suppose that the rate of sorption interaction depends only on the mineral–colloid fraction, i.e., the sorption of Pu ions and its colloidal forms on the i -th mineral colloid will be determined by the same distribution coefficients K_i . The appropriate formalized record has the form:

$$\bar{K}_{ji} = K_i \quad (j = 1; N+2; N+M+1; i = 2, 3, \dots, N+1). \tag{25.8}$$

Actually, $K_i \equiv \bar{K}_{1i}$.

Introduce the denotation

$$S_i = K_i C_i, \tag{25.9}$$

and rewrite Eqs. 25.3–25.5 and 25.7 in the form:

for ionic Pu forms

$$C'_1 = C_1 + \sum_{i=2}^{N+1} S_i C_1; \tag{25.10}$$

for intrinsic Pu colloids

$$\begin{aligned}
 C'_{N+2} &= C_{N+2} + \sum_{i=2}^{N+1} S_i C_{(N+2)}, \\
 C'_{N+3} &= C_{N+3} + \sum_{i=2}^{N+1} S_i C_{(N+3)}, \\
 &\dots\dots\dots, \\
 C'_{N+M+1} &= C_{N+M+1} + \sum_{i=2}^{N+1} S_i C_{(N+M+1)};
 \end{aligned} \tag{25.11}$$

for mineral colloids

$$\begin{aligned}
 C'_2 &= C_2 + S_2 C_1 + \sum_{j=N+2}^{2N+1} S_2 C_j, \\
 C'_3 &= C_3 + S_3 C_1 + \sum_{j=N+2}^{2N+1} S_3 C_j, \\
 &\dots\dots\dots, \\
 C'_{N+1} &= C_{N+1} + S_{(N+1)} C_1 + \sum_{j=N+2}^{2N+1} S_{N+1} C_j.
 \end{aligned} \tag{25.12}$$

The additional system of Pu balance equations in solutions after several (N) stages of membrane filtration:

$$\begin{aligned}
 {}^T C_1^N &= C_1 + \sum_{i=2}^N S_i C_1 + \sum_{i=N+2}^{N+M} C_i + \sum_{j=N+2}^{N+M} \sum_{i=2}^N S_i C_j, \\
 {}^T C_1^{N-1} &= C_1 + \sum_{i=2}^{N-1} S_i C_1 + \sum_{i=N+2}^{N+M-1} C_i + \sum_{j=N+2}^{N+M-1} \sum_{i=2}^{N-1} S_i C_j, \\
 &\dots\dots\dots, \\
 {}^T C_1^1 &= C_1.
 \end{aligned} \tag{25.13}$$

Similarly to (25.6), we can write for the total concentration in solution containing clayey particles

$${}^T C_1^{N+1} = C_1 + \sum_{i=2}^{N+1} S_i C_1 + \sum_{i=N+2}^{N+M+1} C_i + \sum_{j=N+2}^{N+M+1} \sum_{i=2}^{N+1} S_i C_j, \tag{25.14}$$

which is a consequence of Eqs. 25.3 and 25.4.

Thus, we came to the system of Eqs. 25.10–25.13, consisting of $2N + M (= 3N)$ equations and the same number of unknown variables ($2N + M = 3N$):

$$\begin{aligned}
 &S_2, S_3, \dots, S_{N+1}, \\
 &C_2, C_3, \dots, C_{N+1}, \\
 &C_{N+2}, C_{N+3}, \dots, C_{N+M+1},
 \end{aligned}$$

i.e., the system possesses a solution. We assume here that the concentrations $C'_{N+2}, C'_{N+3}, \dots, C'_{N+M+1}$ (25.11) are known: they can be readily evaluated from data of filtration experiments with clay colloid-free liquids. The initial concentrations of individual mineral fractions, $C'_2, C'_3, \dots, C'_{N+1}$ (25.12) are specified based on the results of gravimetric determination of particles with appropriate size retained by various membranes (see Sect. 25.1.2.1). Finally, as mentioned above, the concentrations of ionic Pu forms C'_1 and C_1 are known.

Table 25.3 Observed data and calculated characteristics used for coefficient K_i assessment (pH 6.4–6.9) for different Pu concentrations in solution, $T C_1^{N+1}$

i	Φ_i , nm	$T C_1^{ia}$, $n \cdot 10^9 \text{ gcm}^{-3}$	$T C_1^i$, $n \cdot 10^9$ gcm^{-3}	S_i , —	C_i , $n \cdot 10^6$ gcm^{-3}	K_i , $n \cdot 10^{-5}$ $\text{cm}^3 \text{g}^{-1}$	K^{Aver} , $n \cdot 10^{-5} \text{ cm}^3 \text{g}^{-1}$
$T C_1^{N+1} = 10^6 \text{ BqL}^{-1}$							
5		430	430	1.350	9.47	1.43	
4	400	268	128	0.089	3.29	0.27	
3	200	206	91	0.087	1.95	0.45	0.9
2	100	195	80				
1	5	84 (99 ^b)	39				
$T C_1^{N+1} = 10^5 \text{ BqL}^{-1}$							
5		43	43	2.12	9.66	2.19	
4	400	17.2	6.97	0.21	3.31	0.63	
3	200	15.8	5.46	0.14	1.99	0.70	1.5
2	100	14.3	4.39				
1	5	69 (86 ^b)	2.41				
$T C_1^{N+1} = 10^4 \text{ BqL}^{-1}$							
5		4.30	4.30		9.69	4.71	
4	400	2.69	0.72		3.31	0.62	
3	200	2.35	0.55		1.96	0.46	2.4
2	100	2.18	0.48				
1	5	0.80	0.13				

^aThe weight concentrations were calculated using the relationship: $1 \text{ Bq} = 1.8 \cdot 10^{-12} \text{ M} = 4.3 \cdot 10^{-10} \text{ g}$

^bCorrected data

25.1.2.3 Calculation Results and Parameter Values

In the case of four-step experimental scheme ($N = M = 4$), the original system of Eqs. 25.10–25.13 can be represented in the form of 12 interrelated linear equations, which can be solved by standard mathematical procedures.

The results of estimation of the complex parameter $S_i = K_i C_i$ and the concentrations C_i ($i = 3, 4, 5$) based on the solution of thus reduced system of equations are given in Tables 25.3 and 25.4. Since the concentration of the mineral fraction $5 \text{ nm} < \Phi_2^{\text{Aver}} < 100 \text{ nm}$ is less than 0.1 mg/L , the contribution of particles with $i = 2$ to sorption reactions can be neglected. The obtained values of the sorption distribution coefficient $K_i \equiv K_{di}$ for three different mineral–colloid fractions vary within the range of $(0.3\text{--}4.7) \cdot 10^5 \text{ cm}^3/\text{g}$, when solutions with pH 6.4–6.9 are used and $(0.4\text{--}14) \cdot 10^5 \text{ cm}^3/\text{g}$, when solutions have pH 4.6–5.0.

The obtained partial values of K_i are in agreement with the general knowledge about Pu(IV) sorption on clayey minerals. Moreover, they are in general agreement with the mean values of the sorption distribution coefficient for the entire population of clayey particles (Tables 25.3 and 25.4), which can be evaluated by the formula

Table 25.4 Observed data and calculated characteristics used for coefficient K_i assessment (pH 4.6–5.0) for different Pu content of solution, $T C_1^{N+1}$

i	Φ_i , nm	$T C_1^{ia}$, $n \cdot 10^9 \text{ gcm}^{-3}$	$T C_1^i$, $n \cdot 10^9$ gcm^{-3}	S_i , —	C_i , $n \cdot 10^6$ gcm^{-3}	K_i , $n \cdot 10^{-5}$ $\text{cm}^3 \text{g}^{-1}$	K^{Aver} , $n \cdot 10^{-5} \text{ cm}^3 \text{g}^{-1}$
$T C_1^{N+1} = 10^6 \text{ BqL}^{-1}$							
5		430	430	3.03	9.53	3.20	
4	400	280	176	0.16	3.30	0.48	
3	200	261	159	2.59	1.82	14.2	1.6
2	100	251	73				
1	5	70	8.6				
$T C_1^{N+1} = 10^5 \text{ BqL}^{-1}$							
5		43	43	3.44	9.66	3.56	
4	400	27.2	8.17	0.59	3.30	1.78	
3	200	21.5	3.87	0.15	1.96	0.77	3.8
2	100	20.3	3.01				
1	5	4.47	1.72				
$T C_1^{N+1} = 10^4 \text{ BqL}^{-1}$							
5		4.3	4.3	* ^b	*	NC ^c	
4	400	2.27	2.11	*	*	NC	
3	200	1.64	1.25	*	*	NC	NC
2	100	1.01	1.08				
1	5	0.78	0.69				

^aSee Table 25.3^bNegative roots of the system of Eqs. 25.10–25.13^cThe distribution coefficient was not calculated

$$K^{\text{Aver}} = \frac{T C_1'^2 - T C_1^2}{T C_1^2 \sum_{i=2}^N C_i}, \quad (25.15)$$

following from obvious balance considerations (the numerator in Eq. 25.15 is the drop in concentration in solution because of the sorption of ionic and intrinsic colloidal Pu forms on clayey particles); here $\sum_{i=2}^N C_i$ is the total concentration of clayey particles in the original solution.

With the exception of the results of one of filtration steps, which yielded an anomalously high value of $K_3 \approx 14 \cdot 10^5 \text{ cm}^3/\text{g}$, two general tendencies can be mentioned: (1) a drop in the estimates of K_i with decreasing mean diameter of particles representing the mineral fractions, i.e., $K_5 > K_4 > K_3$, and (2) an increase in the absolute values of coefficient K_i , characterizing the i -th fraction, with a decrease in total Pu concentration in the working solution.

The first tendency seems to demonstrate that the sorption of intrinsic colloids on the surface of mineral aggregates dominates over the sorption of ionic

form: a decrease in clay particle diameter reduces the availability of sorption sites for colloidal Pu forms. The second tendency demonstrates the nonlinearity of the process.

Overall, the laboratory experiments show that the major portion of Pu is retained by the relatively coarse ($i = 5$) mineral fraction ($\Phi_4 = 400\text{ nm}$). This can be attributed to both the higher concentration of colloidal particles with a diameter greater than 400 nm ($C_5' = 9.69\text{ mg/L}$) and the high sorption capacity of this colloidal fraction.

25.2 A Study of Colloidal Forms of Radionuclide Migration at a Radioactive Waste Disposal Site

Groundwater samples were collected at the Tomsk-7 site (Sects. 3.4 and 23.1) from aquifers used for liquid radioactive waste disposal. The samples were ultrafiltered, and the filtrates and various particle size fractions were analyzed for chemical composition and radionuclide activity.

25.2.1 Experimental Setup

Ultrafiltration was carried out with groundwater samples taken

- from observation wells A-3, A-6, A-44 and A-46 within the zone of influence (Table 25.5) of injection of low-level RW (LLW, recharge well cluster 18),
- from observation wells C-66, C-50 and C-37 within the zone of influence (Table 25.6) of injection of intermediate-level RW (ILW, recharge well cluster 18a), Fig. 25.1.

Four-step ultrafiltration (nuclear membranes with pore diameter $\Phi_i = 450, 200, 50$, and 5 nm) was used in the former case, and an experimental three-step scheme (nuclear membranes with pore diameter 400, 50, and 5 nm), in the latter case.

The passage of a water sample through a membrane (Fig. 25.4) results in the retention of a colloidal fraction containing particles with a diameter exceeding the pore diameter of the membrane. As distinct from the experiments with artificial radioactive solutions considered above, the effect of intrinsic colloid formation can be neglected here because of the low radionuclide concentrations in natural waters. Thus, in the case of four-step filtration (Fig. 25.4), after passing through the membrane $\Phi_4 = 450\text{ nm}$, the solution contains radionuclides in the concentration ${}^T C_1^4 = C_1 + C_{12} + C_{13} + C_{14}$; after membrane $\Phi_3 = 200\text{ nm}$, it contains ${}^T C_1^3 = C_1 + C_{12} + C_{13}$; after membrane $\Phi_2 = 50\text{ nm}$, ${}^T C_1^2 = C_1 + C_{12}$; and after membrane $\Phi_1 = 5\text{ nm}$, the solution may be supposed to contain only the ionic forms of radionuclides ${}^T C_1^1 = C_1$. At the same time, colloids successively accumulate on

Table 25.5 Detected ${}^T C_1^N$ ($N = i = 2, 3, 4$), C_1 and calculated values of $\bar{K}_{1i}C_i$ for LLW

Φ_i , nm	i –	U-235		Np-237		Pu-238–240		Am-241	
		${}^T C_1^N$, mgL ⁻¹	$\overline{K}_{1i}C_i$ –	${}^T C_1^N$, mgL ⁻¹	$\overline{K}_{1i}C_i$ –	${}^T C_1^N$, BqL ⁻¹	$\overline{K}_{1i}C_i$ –	${}^T C_1^N$, BqL ⁻¹	$\overline{K}_{1i}C_i$ –
A-46									
450	4	0.8	6.25	$1.4 \cdot 10^{-6}$	2.0	0.58	0.66	0.33	0.89
200	3	0.75	87.25	$1.3 \cdot 10^{-6}$	20.0	0.54	4.43	0.28	2.32
50	2	0.052	5.5	$3.0 \cdot 10^{-7}$	5.0	0.27	3.43	0.15	1.68
5	1	0.008		$5.0 \cdot 10^{-8}$		0.061		0.056	
A-44									
450	4	0.011	0.0	$4.0 \cdot 10^{-6}$	0.22	0.26	0.38	0.0049	0.45
200	3	0.011	4.92	$3.8 \cdot 10^{-6}$	1.65	0.23	0.63	0.0044	1.82
50	2	0.0051	3.25	$2.3 \cdot 10^{-6}$	1.52	0.18	1.28	0.0024	1.18
5	1	0.0012		$9.1 \cdot 10^{-7}$		0.079		0.0011	
A-3									
450	4	0.0041	0.58	$2.0 \cdot 10^{-6}$	0.22	0.038	0.24	0.022	0.0
200	3	0.0038	5.54	$1.9 \cdot 10^{-6}$	1.33	0.034	0.47	0.022	1.37
50	2	$9.2 \cdot 10^{-4}$	0.77	$1.3 \cdot 10^{-6}$	1.88	0.026	0.53	0.015	1.94
5	1	$5.2 \cdot 10^{-4}$		$4.5 \cdot 10^{-7}$		0.017		0.0051	
A-6									
450	4	0.0067	0.83	$4.0 \cdot 10^{-6}$	2.00	0.023	2.50	0.098	0.85
200	3	0.0061	5.56	$2.9 \cdot 10^{-6}$	1.09	0.017	0.83	0.087	1.69
50	2	0.0021	1.92	$2.3 \cdot 10^{-6}$	3.18	0.015	5.25	0.065	4.00
5	1	0.00072		$5.5 \cdot 10^{-7}$		0.0024		0.013	

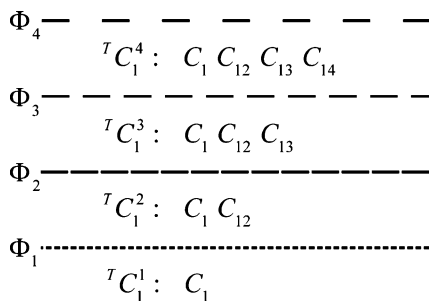
membrane surface: ${}^T C_4 = C_4 + C_{14}$ on membrane $\Phi_3 = 200$ nm, ${}^T C_3 = C_3 + C_{13}$ on membrane $\Phi_2 = 50$ nm, and ${}^T C_2 = C_2 + C_{12}$ on membrane $\Phi_1 = 5$ nm. Here we use the same specification of particles involved in reactions as that used in Sect. 25.1.2.2: C_1 is the concentration of ionic form; C_{1i} is the concentration of the radionuclide adsorbed by the i -th mineral fraction; ${}^T C_i$ is the total concentration of colloids of a fraction; C_i is the concentration of the i -th fraction of colloids in a free form ($i = 2, 3, 4$); ${}^T C_1^N$ is the total concentration; $i = 2$ corresponds to the particles whose size varies within 5 to 50 nm, $i = 3$ corresponds to the range of 50–200 nm; $i = 4$ corresponds to 200–450 nm; the index N corresponds to the maximal index (number) of colloidal fraction. Similar relationships can be obtained for a three-step migration ($i = 2, 3$), where $i = 2$ corresponds to $\Phi_2 = 5$ –50 nm and $i = 3$, to $\Phi_3 = 50$ –400 nm. The concentrations ${}^T C_i$ can be determined analytically: ${}^T C_i = {}^T m_i / V_i$, where ${}^T m_i$ is the mass of the residue on the membrane, V_i is the volume of solution filtered through the membrane.

Table 25.6 Observed ${}^T C_1^N$ ($N = i = 2, 3$), C_1 and calculated values of $\bar{K}_{1i}C_i$ for ILW

Φ_i nm	i —	U		Eu		La		Sr-90	
		${}^T C_1^N$, mgL ^{−1}	$\overline{K}_{1i}C_i$ —	${}^T C_1^N$, mgL ^{−1}	$\overline{K}_{1i}C_i$ —	${}^T C_1^N$, mgL ^{−1}	$\overline{K}_{1i}C_i$ —	${}^T C_1^N$, BqL ^{−1}	$\overline{K}_{1i}C_i$ —
C-66									
400	3	0.5114	18.72	0.28	7.0	0.00051	2.14	101	0.21
50	2	0.4307	98.93	0.077	1.66	0.00021	0.50	85.5	0.13
5	1	0.0431		0.029		0.00014		75.5	
C-50									
400	3	0.0245	2.43	ND ^a		ND		58	0.24
50	2	0.0109	0.95					50.5	0.63
5	1	0.0056						30.95	
C-37									
400	3	0.0445	4.88	0.034	0.57	0.00005	0.25	2.23	1.53
50	2	0.0108	0.57	0.029	2.30	0.00004	0.0	1.29	1.10
5	1	0.0069		0.0088		0.00007		0.615	

^a Radionuclide was not observed.

Fig. 25.4 Progression of solution fractionation during its ultrafiltration through membranes. The experimental conditions under study: $\Phi_4 = 450$, $\Phi_3 = 200$, $\Phi_2 = 50$, $\Phi_1 = 5$ nm



25.2.2 Calculation Algorithm and Obtained Parameter Values

The general system of mass balance equations for radionuclides and mineral colloids, similar to the systems (25.3) and (25.5) considered above, can be written as

$${}^T C_1^N = C_1 + \sum_{i=2}^N C_{1i}, \quad (25.16)$$

$${}^T C_i = C_i + C_{1i}. \quad (25.17)$$

In our case i successively takes on values 4 ($=N$), 3, 2 in the case of four-step filtration (LLW) and 3 ($=N$), 2 in the case of three-step filtration (ILW).

The concentration of the colloidal form of radionuclide C_{1i} is related with the concentration of radionuclides in ionic form C_1 and colloids in solution C_i by the formula (25.1a). Now the system of Eqs. 25.16–25.17 becomes

$${}^T C_1^N = C_1 \left(1 + \sum_{i=2}^N \bar{K}_{1i} C_i \right), \quad (25.18)$$

$${}^T C_i = C_i (1 + \bar{K}_{1i} C_1), \quad (25.19)$$

where $\bar{K}_{1i}$ are partial equilibrium constants, $i = 4 (=N), 3, 2$.

When $N = 6$ (four-step experimental scheme), we come to a system consisting of Eqs. 25.18–25.19. The system includes six unknowns ($\bar{K}_{12}, \bar{K}_{13}, \bar{K}_{14}, C_2, C_3$, and C_4), which can be determined given $C_1, {}^T C_1^2, {}^T C_1^3, {}^T C_1^4, {}^T C_2, {}^T C_3$, and ${}^T C_4$.

Unfortunately, because of the low sensitivity of the gravimetric method of analysis used to find the weights of residue on membranes, we failed to determine the concentrations ${}^T C_i$ ($i = 4, 3, 2$). Therefore, the calculation procedure considered above can be only used to determine the complex parameter $S_{1i} = \bar{K}_{1i} C_i$. To do this, it is sufficient to solve the system of Eqs. 25.18–25.19. The obtained values of $\bar{K}_{1i} C_i$ are given in Tables 25.5 and 25.6.

To obtain an approximate estimate of parameter $\bar{K}_{1i}$, which can be interpreted as a coefficient of sorption distribution, it can be assumed that the total weight concentration of the colloidal fraction does not exceed a few milligrams per liter. Now, $\bar{K}_{1i}$ is of the order of $S_{1i} \cdot 10^6 \text{ cm}^3/\text{g}$. As a first approximation, we can take $\sum_{i=2}^N C_i = 1 \text{ mg/L}$, assuming that all fractions have the same shares in the total weight concentration.

Now the analysis of the obtained data allows us to make the following conclusions: (1) among actinides, uranium has the largest sorption capacity in the given system, its mean coefficient of sorption distribution is about $3 \cdot 10^6 \text{ cm}^3/\text{g}$; (2) plutonium, neptunium, and americium feature lower values of sorption distribution coefficient ($0.4\text{--}1.0$) $\cdot 10^6 \text{ cm}^3/\text{g}$; (3) a general tendency toward an increase in sorption intensity on finer particles is observed; (4) strontium sorption is less intense.

Finally, based on data given in Tables 25.5 and 25.6, we can easily calculate the percent concentrations of radionuclides migrating in colloidal form:

$$C_{\text{RN-COLL}} = \left(1 - \frac{C_1}{{}^T C_1^{A(3)}} \right) \cdot 100\%. \quad (25.20)$$

As can be seen (Table 25.7), the concentration of radionuclides in colloidal form, except for Sr-90, in most cases is above 70–80% of their total amount in water samples.

Thus, the presented modeling approaches for data from membrane ultrafiltration tests analysis allow us to assess the sorption distribution coefficients controlling interactions between radionuclides and colloids of different genesis. Experiments with synthesized solutions, containing high concentrations of Pu ($10^4\text{--}10^6 \text{ Bq/L}$), showed that both pseudocolloids and intrinsic colloids, interacting with each other,

Table 25.7 The amount of radionuclide adsorbed by colloids

LLW								
Well	U		Np		Pu		Am	
	%	BqL ⁻¹	%	BqL ⁻¹	%	BqL ⁻¹	%	BqL ⁻¹
A-46	99.9	0.98	96.4	0.034	89.5	0.519	83.0	0.274
A-44	89.1	0.012	77.5	0.078	69.6	0.181	77.6	0.0038
A-3	87.3	0.0043	77.5	0.039	55.3	0.021	76.8	0.0169
A-6	89.3	0.0074	86.3	0.087	89.6	0.0206	89.7	0.085
ILW								
	U		Eu		La		Sr-90	
	%	BqL ⁻¹	%	BqL ⁻¹	%	BqL ⁻¹	%	BqL ⁻¹
C-66	91.6	0.575	89.6	$6.5 \cdot 10^{-4}$	73.9	$6.5 \cdot 10^{-5}$	25.2	25.5
C-50	77.1	0.023	NA ^a		NA		46.6	27.0
C-37	84.5	0.046	73.9	$6.5 \cdot 10^{-5}$	NA		72.4	1.6

^a No data available

may play a significant role in the overall transport process. The values of plutonium sorption distribution coefficients on mineral particles (<0.001 mm), obtained in experiments with synthesized solutions, are of the order of $10^5 \text{ cm}^3/\text{g}$.

The studies described here also proved the high degree of involvement of colloidal particles at Tomsk-7 site in the formation of the total transport potential of actinides such as Pu and Am. The problem still to be studied is the reversibility of the identified sorption process in the “mineral/inorganic colloids–actinides” system, implying that the studies along this line should be continued. Overall, the obtained data formed the basis for developing migration models, which will be described in the following chapter.

Reference

Zakharova EV, Kaimin EP, Volkova AG et al (2007) Experimental and modeling study of colloid-facilitated transport of radionuclides in aquifers (with application to deep-well radioactive waste disposal at Siberian Chemical Plant). 1 Radionuclide adsorption on colloidal particles. *Geoecology* 1:39–50 (In Russian)

Chapter 26

Models of Sorption Type for Colloid-Facilitated Transport in Aquifers

This chapter considers sorption-based numerical models simulating 1D migration of chemical species in the presence of mobile reactive colloids. One of the model extensions includes a module for simulating the migration of a colloid mixture characterized by heterogeneous distributions of particle size and sorption properties. The modeling analysis is accompanied by simple analytical assessments based on characteristic solutions. The simulation and analytical results indicate that species binding to colloids may lead to a considerable enhancement of the colloid-mediated solute migration. The differences in the kinetic constants for sorption and desorption as well as sorption irreversibility appreciably affect the transport rate at local and regional scales.

26.1 The Governing Equations for Migration of Colloidal Solutions

In previous chapters we considered processes accompanying the migration of a contaminant in the presence of one type of colloids (all colloid particles have the same sorption characteristics). Their models can be referred to the class of dual-species (one colloid plus one contaminant). However, the available experimental material (Chap. 25) gives grounds for the development of migration models for a solution containing several colloidal associations with different sorption activities. The models describing mass transfer in such systems can be classified as polydisperse colloidal models (a colloid population plus one contaminant).

26.1.1 A Dual-Species Model

The general structure of transport differential equation has the form of Eq. 1.25, where concentration C should be understood as partial concentrations of each phase involved in mass flux formation in the moving fluid, and the function $W_s = W_s(P)$ should be associated with the type of sorption interaction (see Sect. 24.3).

Thus, the state of the system under consideration is described by six functions (C_1/S_1 , C_{12}/S_{12} , C_2/S_2), related by equations (Lüthmann et al. 1998; van de Weerd et al. 1998), describing

- the transport and sorption of a dissolved component

$$\phi \frac{\partial C_1}{\partial t} + q \frac{\partial C_1}{\partial x} - \phi D_L \frac{\partial^2 C_1}{\partial x^2} = -P_1^S - P_{12} - P_{12}^S, \quad (26.1)$$

$$\frac{\partial S_1}{\partial t} = P_1^S; \quad (26.1a)$$

- the transport and sorption of a component migrating in colloidal form

$$\phi \frac{\partial C_{12}}{\partial t} + q \frac{\partial C_{12}}{\partial x} - \phi D_L \frac{\partial^2 C_{12}}{\partial x^2} = P_{12} - P^{SC}, \quad (26.2)$$

$$\frac{\partial S_{12}}{\partial t} = P_{12}^S + P^{SC}; \quad (26.2a)$$

- the transport and sorption of the colloidal fraction

$$\phi \frac{\partial C_2}{\partial t} + q \frac{\partial C_2}{\partial x} - \phi D_L \frac{\partial^2 C_2}{\partial x^2} = -P_2^S, \quad (26.3)$$

$$\frac{\partial S_2}{\partial t} = P_2^S; \quad (26.3a)$$

here q is the Darcy velocity [LT^{-1}], ϕ is the porosity [L^3L^{-3}], D_L is the coefficient of longitudinal hydrodynamic dispersion [L^2T^{-1}]. In their right parts, the above equations contain terms accounting for kinetic sorption or desorption of the major phases involved in mass transport.

If we neglect the kinetics of all sorption reactions, then, by summing the left and right parts of equations (26.1)–(26.2) and (26.3a), we will reduce the system of equations (26.1)–(26.2a) to the equation

$$\frac{\partial}{\partial t} (\phi C_1^T + S_1^T) + q \frac{\partial C_1^T}{\partial x} - \phi D_L \frac{\partial^2 C_1^T}{\partial x^2} = 0, \quad (26.4)$$

where the total concentrations are described by expressions

$$\begin{aligned} C_1^T &= C_1 + C_{12}, \\ S_1^T &= S_1 + S_{12}. \end{aligned} \quad (26.4a)$$

In the case of linear sorption, considering (24.16)–(24.19), we have

$$\begin{aligned} C_1^T &= C_1(1 + \bar{K}_{12}C_2), \\ S_1^T &= C_1(\bar{K}_1 + \bar{K}_2\bar{K}_{12}^S C_2). \end{aligned} \quad (26.4b)$$

Further transformations of Eq. 26.4 with the substitution of relationships (26.4b) yield:

$$\begin{aligned} & \left[\phi(1 + \bar{K}_{12}C_2) + \bar{K}_1 + \bar{K}_2\bar{K}_{12}^S C_2 \right] \frac{\partial C_1}{\partial t} + \left(\phi\bar{K}_{12} + \bar{K}_2\bar{K}_{12}^S \right) C_1 \frac{\partial C_2}{\partial t} \\ & + (1 + \bar{K}_{12}C_2) q \frac{\partial C_1}{\partial x} + \bar{K}_{12} q C_1 \frac{\partial C_2}{\partial x} - \phi D_L \\ & \times \left[(1 + \bar{K}_{12}C_2) \frac{\partial^2 C_1}{\partial x^2} + \bar{K}_{12} C_1 \frac{\partial^2 C_2}{\partial x^2} + 2\bar{K}_{12} \frac{\partial C_1}{\partial x} \cdot \frac{\partial C_2}{\partial x} \right] = 0. \end{aligned} \quad (26.5)$$

In the equilibrium linear formulation, the system of equations (26.3)–(26.3a), describing the transport and interaction of colloids with mineral rock matrix, can be generalized to become

$$(\phi + \bar{K}_2) \frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial x} - \phi D_L \frac{\partial^2 C_2}{\partial x^2} = 0 \quad (26.6)$$

(considering that $\partial S_2 / \partial t = \bar{K}_2 \partial C_2 / \partial t$).

26.1.2 Transport of a Polydisperse Colloidal Solution

The model considered bellow is developed to simulate the transport of variably sized colloids and a contaminant in porous media. This model generalizes the sorption-based approach to include the effects of interaction between colloid populations and a contaminant of interest.

If the sorption has a linear character

$$S_{1i} = \bar{K}_i \bar{K}_{1i}^S C_i C_1, \quad (26.7)$$

the total concentrations of a component in solution and solid phase (including precipitated colloids) can be described by the equations

$$\begin{aligned} C_1^T &= C_1 \left(1 + \sum_2^{N+1} \bar{K}_{1i} C_i \right), \\ S_1^T &= C_1 \left(\bar{K}_1 + \sum_2^{N+1} \bar{K}_i \bar{K}_{1i}^S C_i \right), \end{aligned} \quad (26.7a)$$

where $i (= 2, \dots, N + 1)$ is the conventional number of a colloidal association, N is the number of associations, $\bar{K}_i$, $\bar{K}_{1i}$, $\bar{K}_{1i}^S$ are coefficients characterizing the adsorption of colloidal groups and the interaction between components and colloids, colloidal complexes and the solid phase.

In this case, contaminant mass balance equation (26.4) becomes

$$\begin{aligned} & \left[\phi \left(1 + \sum_2^{N+1} \bar{K}_{1i} C_i \right) + \bar{K}_1 + \sum_2^{N+1} \bar{K}_i \bar{K}_{1i}^S C_i \right] \frac{\partial C_1}{\partial t} + C_1 \sum_2^{N+1} \left(\phi \bar{K}_{1i} + \bar{K}_i \bar{K}_{1i}^S \right) \frac{\partial C_i}{\partial t} \\ & + \left(1 + \sum_2^{N+1} \bar{K}_{1i} C_i \right) q \frac{\partial C_1}{\partial x} + C_1 q \sum_2^{N+1} \bar{K}_{1i} \frac{\partial C_i}{\partial x} - \phi D_L \\ & \times \left[\left(1 + \sum_2^{N+1} \bar{K}_{1i} C_i \right) \frac{\partial^2 C_1}{\partial x^2} + C_1 \sum_2^{N+1} \bar{K}_{1i} \frac{\partial^2 C_i}{\partial x^2} + 2 \frac{\partial C_1}{\partial x} \sum_2^{N+1} \bar{K}_{1i} \frac{\partial C_i}{\partial x} \right] = 0. \end{aligned} \quad (26.8)$$

The migration of an i -th association of colloids, whose sorption follows a linear law, can be described by the equation

$$(\phi + \bar{K}_i) \frac{\partial C_i}{\partial t} + q \frac{\partial C_i}{\partial x} - \phi D_L \frac{\partial^2 C_i}{\partial x^2} = 0, \quad i = 2, \dots, N+1. \quad (26.9)$$

The full solution of equations given in this section with appropriate boundary conditions requires the application of numerical methods. The solution implies the calculation of equilibrium partial boundary concentrations C_{i0} from the conditions of chemical (sorption) equilibria in solution given the total concentrations of colloidal particles and contaminants C_{i0}^T (see Sect. 26.3). However, it is reasonable to begin with the consideration of a simplified mathematical formulation of the problem, which allows some analytical estimates to be obtained.

26.2 A Model with Effective Parameters

26.2.1 Equilibrium Reversible Sorption

Simplified estimates can be obtained if we assume that the concentration of colloids remains constant within the pollution zone ($C_2 = \text{const}$). In this case,

$$S_1^T = \frac{\bar{K}_1 + \bar{K}_2 \bar{K}_{12}^S C_2}{1 + \bar{K}_{12} C_2} C_1^T \quad (26.10)$$

and Eq. 26.4 becomes

$$\phi_1^e \frac{\partial C_1^T}{\partial t} + q \frac{\partial C_1^T}{\partial x} - \phi D_L \frac{\partial^2 C_1^T}{\partial x^2} = 0, \quad (26.11)$$

where the effective porosity ϕ_1^e is determined by

$$\phi_1^e = \phi + \frac{\bar{K}_1 + \bar{K}_2 \bar{K}_{12}^S C_2}{1 + \bar{K}_{12} C_2}. \quad (26.11a)$$

If there is no sorption of colloids ($\bar{K}_2 = 0$), we obtain

$$\phi_1^e = \phi + \frac{\bar{K}_1}{1 + \bar{K}_{12} C_2} \equiv \phi + \frac{K_d \rho_b}{1 + K_d^c C_2}, \quad (26.11b)$$

whence it can be readily seen that the presence of colloids, reducing the effective porosity relative to the limiting case ($\phi_1^e = \phi + \bar{K}_1$), enhances the potential of mass transport.

If the coefficients of sorption distribution of a component, which is adsorbed on active and passive (precipitated) colloids, are equal ($\bar{K}_{12} = \bar{K}_{12}^S$), as well as the coefficients $\bar{K}_1$ and $\bar{K}_2$, we have $\phi_1^e = \phi^e$ (the case where there are no colloids in solution). The relationship (26.11b), written as

$$\phi_1^e = \phi + \frac{K_d \rho_b}{1 + K_d F C_2} \quad (26.11c)$$

(see Sect. 24.3.2), shows, in particular, that the colloidal transport becomes significant when $FK_d C_2 > 0.2 - 0.5$. The value of FK_d can reach $N \cdot 10^4 \text{ cm}^3/\text{g}$ (Vilks and Dequellare 1991), i.e., colloidal transport plays an appreciable role in radionuclide transport only when the colloidal particle content of groundwater is sufficiently high ($C_2 > 10 \text{ mg/L}$).

Physically, it is clear that when the solution moves in a homogeneous porous (fractured) medium, the export of particles $M_1 A_2$ beyond the ion adsorption front disturbs the equilibrium and causes the decay of $M_1 A_2$ compound (the colloid loses an ion). The newly formed portion of ions M_1 is spent for saturating the sorption capacity of the immobile mineral phase, making the single front to move with a higher velocity, depending on the stability of $M_1 A_2$ and the concentration in solution of the particles forming it.

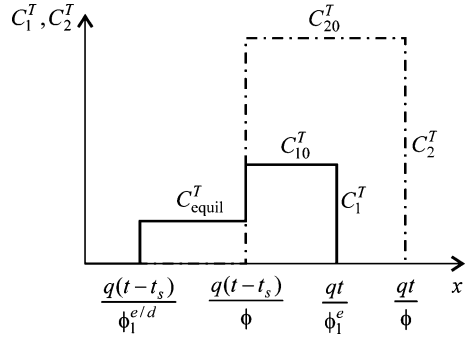
Neglecting variations in C_2 in the case of multicomponent transport, we obtain from Eq. 26.8 an expression for the effective capacity (porosity):

$$\phi_1^e = \phi + \frac{\bar{K}_1 + \sum_{i=1}^{N+1} \bar{K}_i \bar{K}_{1i}^S C_i}{1 + \sum_{i=1}^{N+1} \bar{K}_{1i} C_i}. \quad (26.12)$$

Calculations using Eqs. 26.11a–26.12 are of use in estimating the displacement of leading concentration fronts. However, such transformations are also useful in the description of the formation of desorption waves after the intrusion (at time $t = t_s$) into the bed of clear waters containing neither contaminants ($C_1 = 0$), nor colloidal particles ($C_2 = 0$), when

$$\phi_1^{e/d} = \phi + \bar{K}_1 > \phi_1^e \quad (26.13)$$

Fig. 26.1 Schematic representation of desorption wave formation process during one-dimensional advective transport (without dispersion)



($\phi_1^{e/d}$ is the effective porosity at the desorption front; see, e.g., Eq. 26.11a with $C_2 = 0$). The “passive wave” that forms in this case (Rumynin et al. 1998) has a leading front moving with a velocity $u = q/\phi$ (Fig. 26.1) and an equilibrium concentration C_{equil}^T with

$$\frac{C_{\text{equil}}^T}{C_{10}^T} = \frac{S_1^T}{S_1^{T/d}} = \frac{\bar{K}_1 + \bar{K}_2 \bar{K}_{12}^S C_2 / \bar{K}_1}{1 + \bar{K}_{12} C_2} \quad (26.14)$$

($S_1^{T/d} = \bar{K}_1 C_1^T$ is the concentration of the component on the solid phase in the absence of colloids).

Finally, it should be mentioned that the kinetic of sorption processes, in particular, the irreversible character of the reaction (24.9) can shift estimates made using formulas (26.11a)–(26.12).

26.2.2 Irreversible Sorption

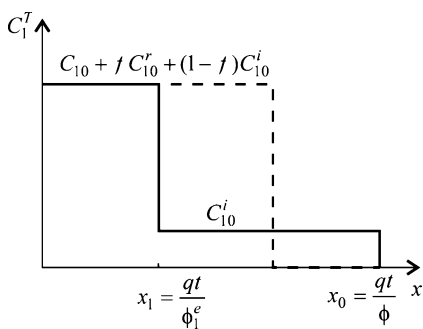
If sorption on *all* colloids occurring in an equilibrium solution at the inlet section of the bed is irreversible, two zones will form in the migration process. The first zone $C_1^T = C_{10} + C_{120}^i$ has a leading boundary moving with the velocity $u_1 = q/(\phi + \bar{K}_1)$. In the second zone, $C_1^T = C_{120}^i$ (here C_{120}^i is the concentration of the component that is irreversibly adsorbed by colloids); its leading front moves with the velocity of water particles $u_0 = q/\phi$, because components cannot be released from the sorption sites on colloids.

Most often, however, the solution contains *two* types of colloids, such that the total concentration in the original solution is

$$C_{120}^T = f C_{120}^r + (1 - f) C_{120}^i, \quad (26.15)$$

where $C_{120}^r = \bar{K}_{12}^r C_{20} C_{10}$ for linear reversible sorption; $\bar{K}_{12}^r$ is the distribution coefficient; f is the relative concentration (fractionation coefficient) of the contaminant, which is adsorbed on colloids in an equilibrium and reversible manner.

Fig. 26.2 To the assessment of sorption irreversibility of components on colloids and the character of concentration front (the *full line*). The *dashed line* is for equilibrium sorption ($f = 1$)



Write the mass balance equation of a component in a streamtube with a unit cross-section (Fig. 26.2), considering that only colloids of the second group are in the leading zone of the flow ($x_0 - x_1$):

$$qC_{10}^T t = x_1 [\phi(C'_{120} + C''_{120} + C_{10}) + \bar{K}_1 C_{10}] + (x_0 - x_1) \phi C''_{120}, \quad (26.16)$$

$C'_{120} = f C_{120}^r$, $C''_{120} = (1-f)C_{120}^i$. Its solution with $x_0 = qt/\phi$ yields

$$x_1 = \frac{qt}{\phi + \bar{K}_1 C_{10} / (C_{10} + f C_{120}^r)}, \quad (26.17)$$

i.e., the effective porosity is described by the equation

$$\phi_1^e = \phi + \frac{\bar{K}_1}{1 + f \bar{K}_{12}^r C_{20}}. \quad (26.17a)$$

If $f = 0$ (all components occur as irreversibly adsorbed), we have $\phi_1^e = \phi + \bar{K}_1$; if $f = 1$, we come to Eq. 26.11b.

This reasoning is rather formal, because the substantiation of the possibility of the coexistence of equilibrium and nonequilibrium migration forms in the same solution requires special model and experimental studies.

26.3 Numerical Modeling and Illustrative Examples

26.3.1 Introduction Comments

The mathematical formulation of the problem considered in Sect. 26.1 was implemented numerically. A finite-difference (explicit and implicit calculation schemes) approximation of the system of equations (26.1)–(26.3) was used in the general case of sorption processes in the kinetic domain, or an approximation of the systems (26.5)–(26.6) and (26.8)–(26.9) in the case of equilibrium linear sorption of dissolved components and colloids.

In the case of an explicit scheme with a central difference the convergence of solution was controlled by the simultaneous meeting of Courant ($Co = q\Delta t / \phi\Delta x \leq 1$), Peclet ($Pe = u\Delta x / D_L \leq 2$), and Fourier ($Fu = D_L\Delta t / (\Delta x)^2 = Co/Pe \leq 1/2$) criteria (Δx is the space step, q is Darcy velocity, D_L is longitudinal dispersion coefficient, ϕ is the porosity). An iteration method was used to solve the problem using an implicit scheme. Since $u\Delta x \leq D_L$, the effect of numerical dispersion in the calculations is minimal, as is confirmed by the comparison of numerical and analytical solutions.

The illustrative examples given below consider the one-dimensional migration of a component in porous medium ($\phi = 0.2$) over a distance of 1 m. The Darcy velocity $q = 0.01$ m/day, the longitudinal dispersion coefficient $D_L = 5 \cdot 10^{-4}$ m²/day. The space and time steps are $\Delta x = 0.001$ m, $\Delta t = 0.0005$ d. Essentially, the model simulates experiments in filtration columns.

The total concentration of the contaminant at the inlet section of the domain is $C_{10}^T = 10^{-3}$ mg/L, the concentration of colloidal particles is $C_{20}^T = 10$ mg/L (or $\sum_2^{N+1} C_{i0}^T = 10$ mg/L in a system containing several, N , colloidal associations, see Sect. 26.1.2). The partial boundary concentrations C_{10} , C_{20} , and C_{120} (C_{1i0}) were derived from the condition of sorption equilibrium in solution.

Thus, in the case of colloids of the same type (the first and second examples – see below Sects. 26.3.2 and 26.3.3), this condition was determined by the system of equations

$$\begin{aligned} C_{10}^T &= C_{10} + C_{120}, \\ C_{20}^T &= C_{20} + C_{120}, \end{aligned} \quad (26.18)$$

where $C_{120} = f(C_{10}, C_{20})$ is determined by Eq. 24.12.

When the system contains N groups of colloid particles with different adsorption properties (see the third and fourth examples in Sect. 26.3.2), the system of equations becomes

$$\begin{aligned} C_{10}^T &= C_{10} \left(1 + \sum_2^{N+1} \bar{K}_{1i} C_{i0} \right), \\ C_{20}^T &= C_{20} (1 + \bar{K}_{12} C_{10}), \\ &\dots\dots\dots, \\ C_{i0}^T &= C_{i0} (1 + \bar{K}_{1i} C_{10}) \end{aligned} \quad (26.19)$$

(the linear type of sorption interaction/isotherm, see Eq. 24.16).

The introduction of condition $C_{10}^T \ll C_{20}^T$ implies that the further analysis will be focused on the description of the migration of components that occur in the source in microconcentrations, as is typical, e.g., of radioactive pollution of groundwater. The initial concentrations are zero ($C_1^0 = C_2^0 = 0$, $C_i^0 = 0$).

All plots (Figs. 26.3–26.8) give concentrations of dissolved components C_1 (full lines) and the total concentration $C_1^T = C_1 + C_{12}$ (dashed lines and hollow circles), as well as colloid concentration C_2 (dash-and-dot lines). The calculation time, $t = 15$ d.

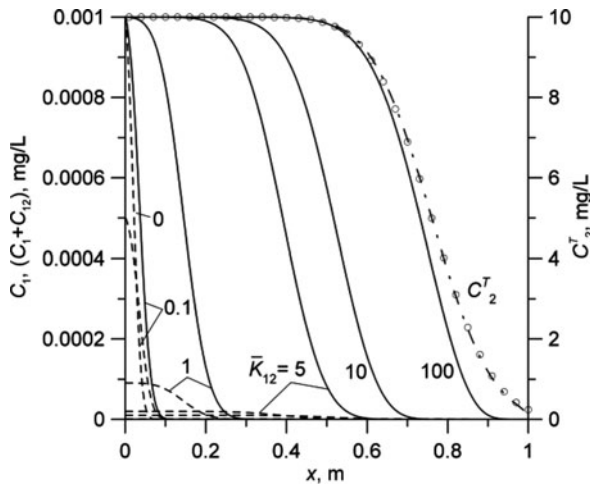


Fig. 26.3 The effect of equilibrium sorption of components on aquifer material and colloids on the concentration distributions $C_1(x)$ (dashed lines, the left axis of the plot) and $C_1^T(x) = C_1 + C_{12}$ (full lines, the same axis). The numbers at curves are the values of the constant $\bar{K}_{12}$ (in L/mg). The calculations were carried out at $\bar{K}_1 = 10$, $\bar{K}_2 = 0$ (there is no sorption of colloids). The dash-and-dot line (the right axis of the plot) is the distribution $C_2^T(x)$, for which an exact (analytical) solution is given (hollow circles)

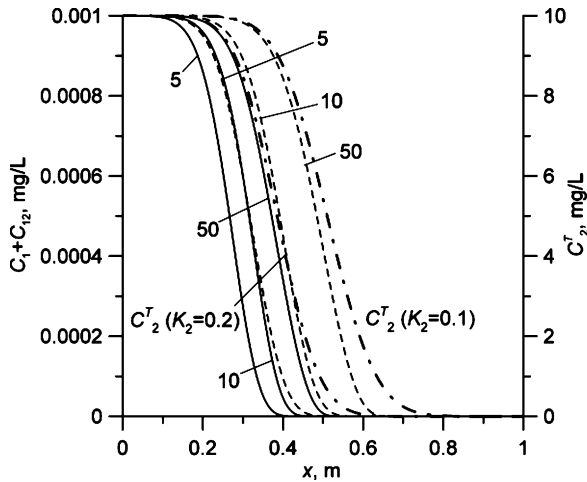


Fig. 26.4 The effect of equilibrium sorption of components on aquifer material and mobile and attached colloids on concentration distributions $C_1^T(x) = C_1 + C_{12}$. The full lines are for $\bar{K}_2 = 0.2$, the dashed lines are for $\bar{K}_2 = 0.1$; the dash-and-dot line is the distribution $C_2(x)$. Numbers at curves are the values of the constant $\bar{K}_{12} = \bar{K}_{12}^S$. The calculations are carried out at $\bar{K}_1 = 10$

26.3.2 Equilibrium Sorption

The examples given below illustrate the effect of various sorption processes on the total potential of mass transport in a system containing colloidal particles.

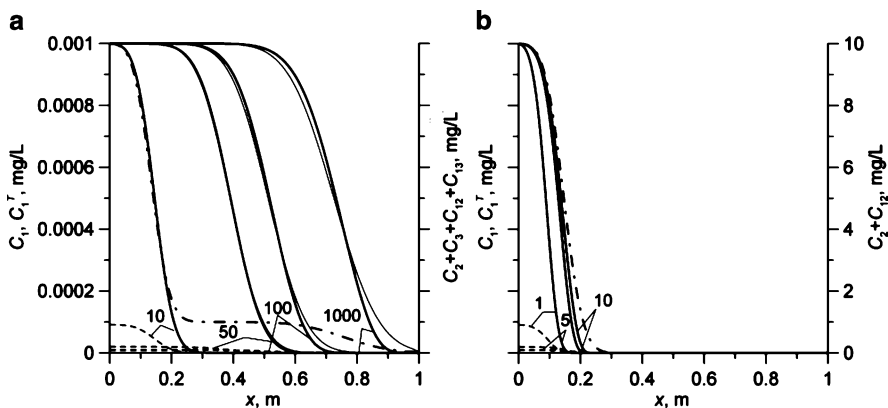


Fig. 26.5 Migration of a component in (a) a solution represented by two groups of colloidal particles and (b) in a solution with effective averaging of sorption interaction parameters. (a) $C_{20}^T = 9 \text{ mg/L}$, $C_{30}^T = 1 \text{ mg/L}$, $\bar{K}_2 = 1.0$, $\bar{K}_3 = 0$, $\bar{K}_{12} = 0$, $\bar{K}_{13} = 10\text{--}1000 \text{ L/mg}$ are the numbers at curves; (b) $\bar{K}_2^{\text{Aver}} = 0.9$, $\bar{K}_{12}^{\text{Aver}} = 1\text{--}10 \text{ L/mg}$ are the numbers at curves, Eq. 26.20; $\bar{K}_1 = 10$. The dashed lines are for C_1 , the full lines are for C_1^T , the dash-and-dot lines are for the total concentration of colloids. The full thin lines are for the solution of Eq. 26.11

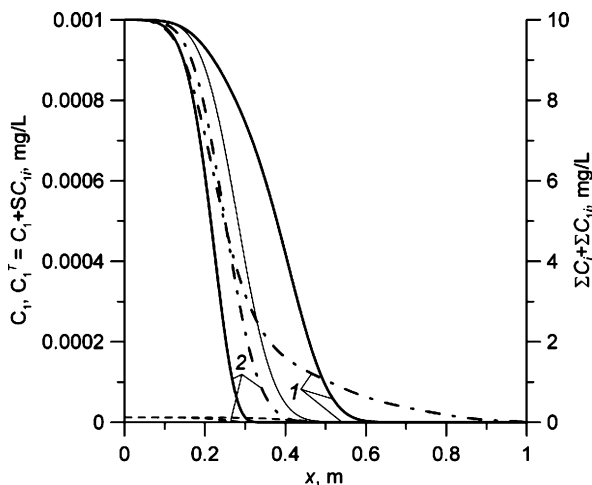


Fig. 26.6 Comparison of concentration distributions during migration of (1) solutions containing five colloidal groups with (2) appropriate estimates obtained for a solution with a single colloid and averaged sorption characteristics. $\bar{K}_1 = 10$; other parameters are given in Table 26.1. The dashed lines are C_1 . Other notations see in Fig. 26.5

The first example in this calculation series (Fig. 26.3) assumes the negligible role of colloid adsorption on the aquifer material ($\bar{K}_2 = 0$); it is however assumed that the colloids themselves can actively adsorb the dissolved component (the parameter $\bar{K}_{12} \equiv K_d^c$ varied within a wide range, from 0.1 to 100 L/mg, $K_d^c = 10^5\text{--}10^8 \text{ cm}^3/\text{g}$);

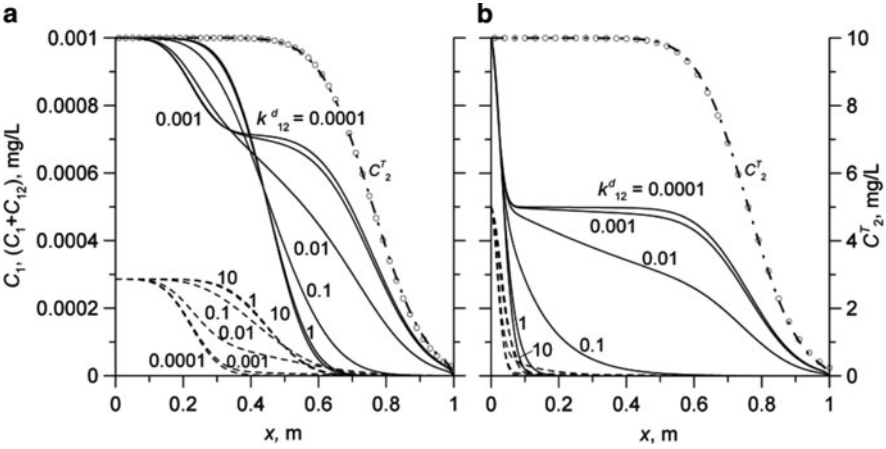


Fig. 26.7 The effect of sorption–desorption kinetics of components during their interaction with colloids on the concentration distributions $C_1(x)$ (dashed lines) and $C_1^T(x) = C_1 + C_{12}$ (full lines). (a) $k_{12}^a = 10 \text{ L(mgd)}^{-1}$, $k_1^d = 20 \text{ d}^{-1}$, $k_{12}^a/k_{12}^d = 0.25 \text{ L/mg}$; (b) $k_1^a = 10 \text{ L(mgd)}^{-1}$, $k_1^d = 1 \text{ d}^{-1}$, $k_{12}^a/k_{12}^d = 0.1 \text{ L/mg}$. The numbers at curves are the values of desorption kinetic constant $k_{12}^d (\text{d}^{-1})$; $S_1^T = 1 \text{ mg/L}$, $S_2^T = 0$, $\bar{C}_{12}^T = 1$, $\bar{S}_{12}^T = 0$. The dash-and-dot line is the distribution of nonsorbable colloids $C_2^T(x)$; an exact (analytical) solution for this distribution is given in the plot by hollow circles

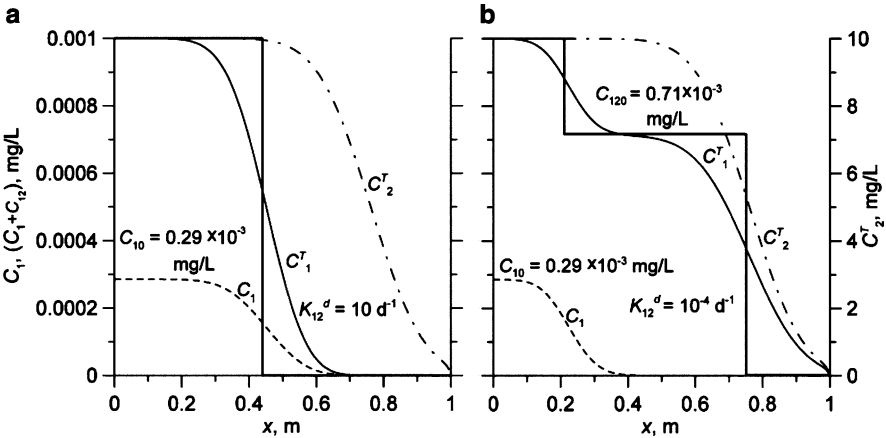


Fig. 26.8 Comparison of numerical and analytical calculations for (a) equilibrium and (b) irreversible sorption

for comparison, the case of $\bar{K}_{12} = 0$ with no sorption on colloids is given. Additionally, the degree of component sorption by solid face was controlled by a dimensionless distribution coefficient $\bar{K}_1 = 10$; the latter value corresponds to a dimensional value $K_d = \bar{K}_1 / \rho_b$ (ρ_b is aquifer material density).

As can be easily seen in Fig. 26.3, the sorption of the component by colloids accelerates the motion of the concentration front of C_1^T , where this concentration is mostly represented by complex C_{12} ($\gg C_1$ at $\bar{K}_{12} \gg 1 \text{ L/mg}$). When $\bar{K}_{12} \geq 100 \text{ L/mg}$, the solution contains practically no ionic form of transport and the pollution front moves with the velocity of nonsorbable colloids (in this case, an inert solute).

It can be easily shown that the calculated capacity of the system ϕ_1^e , which controls the motion of piston-like displacement fronts $x^0 \equiv x|_{\bar{c}=0.5} = qt/\phi_1^e$, can be almost exactly described by the formula Eq. 26.11b. This can be attributed, in particular, to the sorption processes taking place in the domain $C_2 \approx \text{const}$ ($= C_{20} \approx C_{20}^T$).

Unlike the first one, *the second example* takes into account the presence of equilibrium precipitation of colloids ($\bar{K}_2 = 0.1$ and 0.2) and the sorption of components on colloids accumulated in solid phase ($\bar{K}_{12}^S = \bar{K}_{12} = 5\text{--}50 \text{ L/mg}$). As could be expected (Fig. 26.4), an increase in sorption capacity with respect to components in dissolved and colloidal forms leads to a drop in the migration rate of the solute, whose frontal velocity (piston-like displacement) is controlled by parameter ϕ_1^e , calculated from Eq. 26.11a. It is notable that an increase in the constant $\bar{K}_{12}$ ($= \bar{K}_{12}^S$) brings the migration fronts of colloids and dissolved components closer to one another (the concentration of the component in solution, including both ionic and colloidal form is meant here). In the limit ($\bar{K}_{12} \rightarrow \infty$), a single transport front will form (Fig. 26.4).

The third example illustrates contaminant transport ($i = 1$) in the presence of two functional groups of colloids ($i = 2, 3$). Figure 26.5a gives the results of calculations carried out for the migration of a solution containing colloids that are readily adsorbed on solid phase (the total concentration on the boundary $C_{20}^T = 9 \text{ mg/L}$), $\bar{K}_2 = 1.0$, but with low retaining capacity $\bar{K}_{12} = 0$, and nonsorbable colloids, $\bar{K}_3 = 0$ ($C_{30}^T = 1 \text{ mg/L}$), with relatively high retaining capacity, $\bar{K}_{13} = 10\text{--}100 \text{ L/mg}$. In all variants, $\bar{K}_1 = 10$. Calculation results show that, notwithstanding the low concentration C_{30}^T , the overall potential of mass transport is largely determined by the presence of this group of colloids.

The calculations made for the same conditions, but within the framework of a model of a “homogeneous” colloidal mixture (Fig. 26.5b) with averaged parameters

$$\bar{K}_2^{\text{Aver}} = \frac{\sum_{i=2}^N \bar{K}_i C_{i0}^T}{\sum_{i=2}^N C_{i0}^T}, \quad \bar{K}_{12}^{\text{Aver}} = \frac{\sum_{i=2}^N \bar{K}_{1i} C_{i0}^T}{\sum_{i=2}^N C_{i0}^T} \quad (26.20)$$

(in this case, $N = 3$, $\bar{K}_2^{\text{Aver}} = 0.9$, $\bar{K}_{12}^{\text{Aver}} = 1 \text{ L/mg}$ (averaging at $\bar{K}_{13} = 10 \text{ L/mg}$), $\bar{K}_{12}^{\text{Aver}} = 5 \text{ L/mg}$ (at $\bar{K}_{13} = 50 \text{ L/mg}$), $\bar{K}_{12}^{\text{Aver}} = 10 \text{ L/mg}$ (at $\bar{K}_{13} = 100 \text{ L/mg}$)), radically differ from the previous results: the obtained values of the displacement velocity of concentration fronts were dramatically underestimated throughout the range of accepted parameters $\bar{K}_{12}^{\text{Aver}}$.

Table 26.1 The values of C_{i0}^T , $\bar{K}_i$ and $\bar{K}_{1i}$ ($= K_{1i}^S$) for a colloidal “mixture”

i	$C_{i0}^T, \text{mgL}^{-1}$	$\bar{K}_i$	$\bar{K}_{1i}, \text{Lmg}^{-1}$
2	0.5	0.0	100
3	1.0	0.1	10
4	2.0	0.3	5
5	5.0	0.5	2
6	1.5	0.7	1
Mean (Eq. 26.20)		0.425	8.15

A much more acceptable result was obtained by solving Eq. 26.11 with the effective porosity (Fig. 26.5a) determined by formula 26.12; some deviations in the model solution can be seen only at very high values of constant $\bar{K}_{13}$.

The fourth example also illustrates the effect of the heterogeneity of the properties of colloid mixture ($N = 6$, Table 26.1) on the rate of mass transport (Fig. 26.6). As can be seen, the presence in solution of a relatively small amount of particles with higher sorption activity (with respect to the component-contaminant) leads to an appreciable increase in the displacement velocity of the general concentration front, relative to the estimates based on averaged (26.20) parameters (for solutions with a single type of colloids). The calculations based on model (26.11) with effective parameter ϕ_1^e also yield incredibly low rates of concentration front displacement C_1^T (Fig. 26.6), the fact that can be attributed to considerable variations in functions C_i , at which the assumptions forming the basis of the model Eq. 26.11 do not work.

Thus, the heterogeneity of the colloidal mixture, associated with the presence in solution of particles with low concentrations but high sorption capacity, can abruptly accelerate the migration of pollution in aquifers.

26.3.3 The Influence of Sorption Kinetics

The previous model estimates showed that sorption on colloids can appreciably enhance the potential of mass transport. However, if we use the real values of equilibrium constants and the concentration of colloids in groundwater, we will most often find that the increase in the displacement velocities of concentration fronts is not significant. This conclusion follows from the assumption that sorption is equilibrium, according to which the contaminant-carrying colloids very quickly unload it after reaching the clear-water zone at the leading front. The situation may radically change if sorption–desorption processes are not equilibrium, especially if sorption is irreversible.

The aim of this section is to assess the effect of kinetic factor, namely, differences between the kinetic constants of sorption, k_{12}^a , and desorption, k_{12}^d , characterizing the interaction between solutes and colloidal particles, on the rate of within-pore mass transport. The possibility of such differences, confirmed by experiments, was mentioned in Sect. 24.3.3.2.

In the numerical experiment given below, the sorption of components on the solid phase according to Langmuir isotherm (24.13) was considered in the nearly-equilibrium formulation $K_1 = k_1^a/k_1^d = 0.5$ (the *first* variant) and 10 L/mg (the *second* variant) (because of the high absolute values of kinetic constants $k_1^a = 10 \text{ L(mg d)}^{-1}$, $k_1^d = 20 \text{ d}^{-1}$ (the *first* variant) and $k_1^a = 10 \text{ L(mg d)}^{-1}$, $k_1^d = 1 \text{ d}^{-1}$ (the *second* variant)), $S_1^T = 1 \text{ mg/L}$, i.e. $\bar{K}_1 = K_1 S_1^T = 0.5$ (the *first* variant) and 10 (the *second* variant). The sorption of colloids was neglected ($S_2^T = 0$).

In all model calculations (Fig. 26.7), the ratio $K_{12} = k_{12}^a/k_{12}^d = 0.25 \text{ L/mg}$ (the *first* variant) and 0.1 L/mg (the *second* variant), and the constants $\bar{C}_{12}^T = 1$, $S_1^T = 1 \text{ mg/L}$, Eqs. 24.12 and 24.14, were assumed not changing; however, the absolute values of kinetic constants varied within wide ranges: $k_{12}^a = 2.5\text{--}2.5 \cdot 10^{-5} \text{ L(mg d)}^{-1}$ (the *first* variant) and $k_{12}^a = 1\text{--}10^{-5} \text{ L(mg d)}^{-1}$ (the *second* variant), $k_{12}^d = 10\text{--}10^{-4} \text{ d}^{-1}$.

Analysis of the plot (Fig. 26.7) shows that a decrease in the kinetic rate of sorption processes leads to an increase in the potential of mass transport. An appreciable increase in the transfer rate of components adsorbed on colloids was recorded at $k_{12}^d < 0.1 \cdot \text{d}^{-1}$; when $k_{12}^d < 0.01 \cdot \text{d}^{-1}$, pollutant migration velocities on the leading front approach the migration velocities of water particles.

In addition to the model analysis, we give a comparison of numerical (the *first* calculation variant) and analytical solutions (piston-like displacement model) for two limiting cases: the sorption and desorption kinetics is high (Fig. 26.8a) and a very low adsorption–desorption activity of colloids (Fig. 26.8b). In the former case, the velocity of concentration fronts C_1 and C_1^T is controlled by the effective porosity ($\phi_1^e = 0.34$), determined from Eq. 26.11b. In the latter case, function C_1^T is characterized by two fronts: the first is associated with the boundary ($C_1^T = C_{10} + C_{120}$) and moves with the velocity determined by the effective porosity $\phi + \bar{K}_1 (= 0.7)$; the second, leading front is such that $C_1^T = C_{120}$ between it and the rear front. Since colloids are not adsorbed and have not enough time to release (desorb) the component, the leading front moves with the velocity of migration of an inert particle, $u = q/\phi$.

Thus, as could be expected, the low desorption kinetics from the surface of colloidal particles radically increases the hazard of groundwater pollution. In the general case, the estimates of the significance of kinetic factor should be coordinated with the space and time extent of process consideration.

A useful criterion in this case is the Damköhler number (Haggerty and Gorelick 1995; van de Weerd et al. 1998; Bethke 2008)

$$D_k = k_{12}^d L \phi / q,$$

which reflects the ratio of the rate of chemical reaction (mass exchange) to the advective flow velocity (L is the characteristic length of transport). When $D_k > 100$,

the process is close to equilibrium. In our example, the value of D_k varies within the range $2 \cdot 10^{-3}$ – $2 \cdot 10^2$, depending on the value of coefficient k_{12}^d . When $D_k < \approx 0.01$ the process at the given scale (L) of its consideration can be assumed irreversible.

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Chapter 27

A Thermodynamics-Based Conceptual Model for Colloid-Facilitated Solute Transport

As mentioned above (Sect. 19.1.2), changes in the physicochemical conditions in the system over space and time, which take place in unsteady-state migration flows, reduce the potential of the above-considered sorption isotherm-based models with time-invariant coefficients, in particular, models describing colloid-facilitated transport. Their empirical nature does not allow them to be applied outside of the specific parameters of the contaminated site. Therefore, thermodynamics-based approach, describing sorption as a series of specific reactions between dissolved ions and surface sites, can be more productive for analyzing solute transport under field conditions.

When choosing migration models of components associated with colloidal particles, one should take into account that these particles have high surface charges. These charges form an electric field around the particles, such that the adsorption of the charged contaminant ions and ions of background electrolyte on them is controlled by electrostatic interactions, which, in particular, change the activity of ions taking part in adsorption reactions near the mineral surface. Therefore, the most suitable for describing the colloid transport components will be the models that take into account such electrostatic interactions, in particular, the *surface complexation models* (SCMs). Being incorporated in transient solute transport models they allow one to account for the influence of current transformations in groundwater chemistry (in particular, changes in the pH and ionic strength of water) on the transport potential of contaminants.

27.1 Surface Complexation Models (Static Formulation)

In the 1970s and 1980s, much effort was made to develop theoretical models of adsorption (sorption) at the mineral–water interface. A surface complexation modeling approach turned out to be among the most productive and experimentally validated approaches (Davis et al. 1978; Hayes and Leckie 1987; Davis and Kent 1990; Allison et al. 1991; Goldberg 1995; Banwart 1997; Appelo and Postma 2005). The key of the SCMs is to account for chemical reactions in a manner similar to a complexation reaction in a solution.

In classical surface complexation theory, adsorption is described in terms of a set of complex formation reactions between dissolved solutes and *surface functional groups*, SOH, with S denoting a metal from solid structure, located at the solid–liquid interface, and with OH representing a reactive surface hydroxyl bounding to a metal ion, S. Surface functional groups influence the electrical properties of the interface, and their density controls the sorption capacity. Another essential assumption is the diprotic acid model used to describe a combination of equilibrium protonation (SOH_2^+) and deprotonation (SO^-) complexation reactions:



Surface adsorption of ions is described by complexation reactions as well, for example:

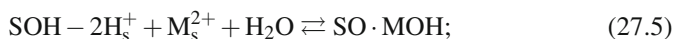
– for a univalent cation



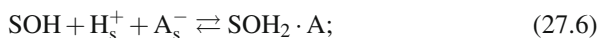
– for a bivalent cation



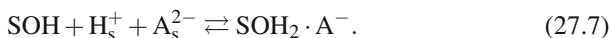
or, if this cation participates in an adsorption–hydrolysis type of reaction,



– for a univalent anion



– for a bivalent anion



Here M^{z+} is a metal ion of charge $z+$, and A^{z-} is a ligand ion of charge $z-$; the subscript s refers to a surface species. Thus, the SCMs treat ion adsorption as complexation reactions analogous to complex formation in solution (Goldberg 1995). The equilibrium constants for these surface reactions are determined by fitting available potentiometric titration and sorption data.

These types of interaction are assumed typical of mineral media represented by oxides (e.g., SiO_2 and Al_2O_3) and amorphous iron oxides (with the general chemical formula $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$), gradually transforming into goethite $\alpha\text{-FeOOH}$ (Dzombak and Morel 1990; Banwart 1997). Amorphous iron oxides (denoted by the conventional abbreviation HFO – hydrous ferric oxides) are substances with

loose crystalline structure and high specific surface ($200\text{--}750\text{ m}^2/\text{g}$). The value and the sign of the charge on the contact surface between HFO and aqueous solutions depend on the medium's pH. HFO are widespread components of rock (sediment) composition. They are very active sorbents and hence play an important role in the formation of sorption properties of rocks, composing the aeration zone and aquifers. HFO precipitation at hydrochemical barriers can be accompanied by coprecipitation of some other pollutants, resulting in groundwater self-purification. The above considerations explain the keen interest to HFO, the adsorption on which can be described within the framework of models of surface complex formation (Dzombak and Morel 1990; Tiffreau et al. 1994).

Thus, the surface complexes of hydroxyl functional groups >SOH^0 are represented by >FeOH^0 (for HFO) and >SiOH^0 (for SiO_2).

From the representation form of reactions (27.1) through (27.7), it can be seen that surface complex formation explains the dependence of sorption rate on pH, which was observed in experiments, meaning that this model hardly has an alternative in this respect. As the result, the model of surface complex formation is gaining wide recognition in the practice of hydrogeological calculations, especially, those involving the prediction of groundwater pollution by radionuclides and heavy metals (Dzombak and Morel 1990; Apak 2006; Turner et al. 2006).

The surfaces of many minerals and oxides carry a charge that depends on pH and the composition of the solution. Therefore the sorption of ions onto the charged surfaces occurs under the influence of electrostatic potential, ψ , specifying contrast in ion activity in the solution, $[i^{\pm}]$, and onto the charged mineral surface, $[i_s^{\pm}]$.

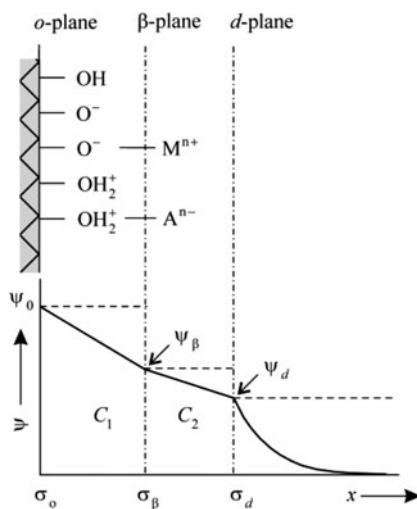
To account in a proper way for this charge effect, additional terms have been introduced into adsorption models, modifying the activity of sorbate ions. These terms describe the electrical work necessary to penetrate the zone of electrostatic potential, resulting in a difference between the activities of ions:

$$[i_s^{\pm}] = [i^{\pm}] \left(e^{-\psi F/RT} \right)^{\pm z} \equiv [i^{\pm}] \left(e^{-e\psi/kT} \right)^{\pm z} \quad (27.8)$$

where F is *Faraday's number* ($= eN_A = 9.64935 \cdot 10^4 \text{ C} \cdot \text{mol}^{-1}$; $e = 1.602 \cdot 10^{-19} \text{ C}$ (Coulomb) is the elementary charge; $N_A = 6.0225 \cdot 10^{23} \text{ mol}^{-1}$ is *Avogadro's number*); R is the *universal gas constant* ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$); k is *Boltzmann's constant* ($= R/N_A = 1.3806 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$); T is the absolute temperature (K); z is the ion charge. The exponent term, $e^{-\psi F/RT}$ is often called “*Boltzmann factor*”.

Clearly, the further calculations of the hydrochemical state of the system, containing adsorbable components, should be associated with the choice (substantiation) of an electrostatic scheme, allowing the effective values of potential, ψ , to be evaluated. The most representative is the *triple-layer model* (Hayes and Leckie 1987; Davis and Kent 1990; Dzombak and Morel 1990; Appelo and Postma 2005). The model assumes three planes of charge denoted o -, β -, and d -planes (Fig. 27.1). The innermost, or o -plane, incorporates the protonation or deprotonation of surface sites. All other specifically adsorbed ions are assigned to the outer or β -plane. Therefore, each plane has its own charge and potential. In the triple-layer approach, weakly bounded ions are modeled as outer-sphere (ion-pair) complexes and strongly bonded ions as inner-sphere (surface coordination) complexes (Hayes et al. 1988).

Fig. 27.1 Conceptual presentation of electrostatic field of the surface–solution interface and positioning of ions for the triple layer model



Two capacitance densities are required to represent the relationship between surface charge and surface potential. The inner-layer capacitance, C_1 , relates the charge and potential between the o -plane and the β -plane. The outer-layer capacitance, C_2 , relates the charge and potential between the β -plane and the d -plane. Potentials ψ_o , ψ_β and ψ_d characterize the electrical field of the charged mineral surface (Fig. 27.1).

The first step to obtaining a closed system of equations describing the interrelated physicochemical and electrostatic equilibria is a transformation of equilibrium equations, e.g., reactions (27.1) through (27.7), into equations for appropriate equilibrium constants, taking into account the correction equality (27.8); in accordance with this equality, the activity of each component is controlled by either potential $\psi = \psi_o$ or potential $\psi = \psi_\beta$.

Thus, according to the law of mass action, the equilibrium constant corresponding to the surface reaction of protonation (27.1) is defined as:

$$K = \frac{[\text{SOH}_2^+]}{[\text{SOH}][\text{H}_s^+]} \quad (27.9)$$

(surface protonation constant). The activity of hydrogen ion on the o -plane, ensuring the involvement of this component in reactions of surface complex formation according to (27.8), will be $[\text{H}_s^+] = [\text{H}^+]e^{-\psi_o F/RT}$; this yields

$$K = \frac{[\text{SOH}_2^+]}{[\text{SOH}][\text{H}^+][e^{-\psi_o F/RT}]} \quad (27.10)$$

Similarly, it can be shown that for the deprotonation reaction (27.2), we have the equality:

$$K = \frac{[\text{SO}^-][\text{H}^+][e^{-\Psi_o F/RT}]}{[\text{SOH}]} \quad (27.11)$$

In a similar manner, we can write equations for reactions involving cations and anions on the β -plane. Thus, for reaction with the participation of an univalent cation (27.3), where $[\text{H}_s^+] = [\text{H}^+]e^{-\Psi_o F/RT}$ and $[\text{M}_s^+] = [\text{M}^+]e^{-\Psi_\beta F/RT}$, we have

$$K = \frac{[\text{SO} \cdot \text{M}][\text{H}^+][e^{-\Psi_o F/RT}]}{[\text{SOH}][\text{M}^+][e^{-\Psi_\beta F/RT}]} \quad (27.12)$$

Next, for adsorption reactions involving bivalent cations $[\text{M}_s^{2+}] = [\text{M}^{2+}][e^{-\Psi_\beta F/RT}]^2$,

$$K = \frac{[\text{SO} \cdot \text{M}^+][\text{H}^+][e^{-\Psi_o F/RT}]}{[\text{SOH}][\text{M}^{2+}][e^{-\Psi_\beta F/RT}]^2} \quad (27.13)$$

Finally, for reactions (27.5), (27.6), and (27.7) we have:

$$K = \frac{[\text{SO} \cdot \text{MOH}][\text{H}^+]^2[e^{-\Psi_o F/RT}]^2}{[\text{SOH}][\text{M}^{2+}][e^{-\Psi_\beta F/RT}]^2} \quad (27.14)$$

$$K = \frac{[\text{SOH}_2 \cdot \text{A}][e^{-\Psi_\beta F/RT}]}{[\text{SOH}][\text{A}^-][\text{H}^+][e^{-\Psi_o F/RT}]} \quad (27.15)$$

$$K = \frac{[\text{SOH}_2 \cdot \text{A}^-][e^{-\Psi_\beta F/RT}]^2}{[\text{SOH}][\text{A}^{2-}][\text{H}^+][e^{-\Psi_o F/RT}]} \quad (27.16)$$

In Eqs. 27.9 through 27.16, the coefficient K is a generalized symbol for the intrinsic equilibrium constants describing the surface complexation reactions.

Thus, in the SCM approach, a coulombic correction is incorporated into the mass action expressions for surface reactions to extract the intrinsic equilibrium constants that are independent of surface charge.

As was the case with standard hydrochemical reasoning for systems containing dissolved ionic associations and ions forming them, the above relationships are supplemented by the balance equation

$$[\text{SOH}]^T = [\text{SOH}] + \sum_{i=1}^M y_{\text{Si}}, \quad (27.17)$$

where $[\text{SOH}]^T$ is the total concentration of the active sorption sites; y_{Si} is the concentration of sites associated with the i -th sorbing particle.

For example, for a system containing univalent ions M^+ and A^- , we have:

$$[\text{SOH}]^T = [\text{SOH}] + [\text{SOH}_2^+] + [\text{SO}^-] + [\text{SO} \cdot \text{M}] + [\text{SOH}_2 \cdot \text{A}]. \quad (27.18)$$

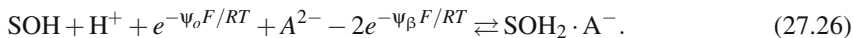
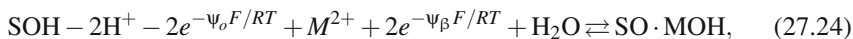
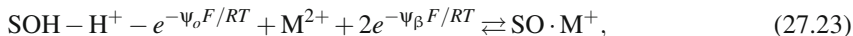
The concentration of $[\text{SOH}]^T$, expressed in moles per liter (dm^3), can be calculated as

$$[\text{SOH}]^T = N_{\text{SA}} S_{\text{A}} C_{\text{S}}, \quad (27.19)$$

where N_{SA} is the surface site density (mol/dm^2), $N_{\text{SA}} = N_{\text{S}}/N_{\text{A}}$, N_{S} is the analytically determined adsorption site density (sites/m^2), N_{A} is the Avogadro number ($6.02205 \cdot 10^{23} \text{ mol}^{-1}$); S_{A} is the surface reduced to unit of weight of the solid phase (dm^2/kg); C_{S} is the concentration of the solid phase (kg/dm^3). N_{SA} for a sorbing surface is determined by regressing experimental data (e.g., from acid-base titration). The concentration C_{S} for colloidal suspension can be measured, and the concentration C_{S} for rock matrix is ρ_b/ϕ (ρ_b is rock density, kg/dm^3 , ϕ is porosity).

The characteristic values of S_{A} (in m^2/g) for some natural minerals (Santamarina et al. 2002) are 400–800 for montmorillonite, 80–100 for illite, 10–20 for kaolinite, and 140–170 for attapulgite.

To make mathematical operations more convenient and to preserve the homogeneity of calculation algorithms in modeling, a concept of “electrostatic” component is introduced, representing some “virtual” particle (Boltzmann particle) with an activity of $[e^{-\psi F/RT}]$. The analysis of equations for equilibrium constants, (27.10) through (27.16), gives the following reactions, being analogues of basic reactions (27.1) through (27.7),



Thus, the reactions of surface complex formation can be described similarly to ordinary complex formation reactions in liquid phase with the incorporation of electrostatic particles in these reactions. Their concentrations (activities) are calculated from the following electrostatic considerations.

Let us assume that surface charge densities in o -, β - and d -planes are σ_o , σ_β , and σ_d (Fig. 27.1), and electrical capacitance between o - and β -planes is defined as C_1 , and between β - and d -planes, as C_2 . The net surface charge density, σ_s , corresponding to the charge fixed to the surface, is opposite in sign to that in the diffusive layer, σ_d , or $\sigma_s = -\sigma_d = \sigma_o + \sigma_\beta$, allowing us to write the charge balance expression

$$\sigma_o + \sigma_\beta + \sigma_d = 0. \quad (27.27)$$

The relationships between potentials are based on the constant capacitance concept (Goldberg 1995; Kallay and Žalac 2001):

$$\begin{aligned}\sigma_o &= C_1(\psi_o - \psi_\beta), \\ \sigma_\beta &= C_1(\psi_\beta - \psi_o) + C_2(\psi_\beta - \psi_d), \\ \sigma_d &= C_2(\psi_d - \psi_\beta);\end{aligned}\tag{27.28}$$

the dimension of electrical charge densities, σ_o , σ_β and σ_d , is C dm^{-2} , the dimension of electrical capacitances, C_1 and C_2 is F dm^{-2} , and the dimension of electrical potentials, ψ_o , ψ_β and ψ_d is V. The value of the inner-layer capacitance density is adjusted to find the value that optimizes the fit of the exponential data. Capacitance C_2 is usually fixed in the range between $0.1 \cdot 10^{-2}$ and $0.2 \cdot 10^{-2} \text{ F dm}^{-2}$.

The charge of α - and β -planes is defined as the sum of associated surface complexes (Yeh et al. 1995):

$$B\sigma_o = \sum_{i=1}^M a_{io}^y [y_{si}],\tag{27.29}$$

$$B\sigma_\beta = \sum_{i=1}^M a_{i\beta}^y [y_{si}],\tag{27.30}$$

where a_{io}^y and $a_{i\beta}^y$ are stoichiometric coefficients for electrostatic components, $e^{-\psi_o F/RT}$ and $e^{-\psi_\beta F/RT}$, in the appropriate reactions of surface complex formation; B is the coefficient of conversion from the charge measurement unit per unit area to mole per unit volume, $B \sim S_A C_S / F$ (mol/C dm) (27.19).

For example, in the case of simplest reactions of surface complex formation (27.20) through (27.22) and (27.25), we have (Kallay and Žalac 2001):

$$B\sigma_o = [\text{SOH}_2^+] + [\text{SOH}_2 \cdot \text{A}] - [\text{SO}^-] - [\text{SO} \cdot \text{M}],\tag{27.31}$$

$$B\sigma_\beta = [\text{SO} \cdot \text{M}] - [\text{SOH}_2 \cdot \text{A}].\tag{27.32}$$

The Gouy–Chapman theory, developed for univalent electrolytes, provides the relationship between the surface charge density, σ_s , and the potential at the onset of the diffuse layer, ψ_d :

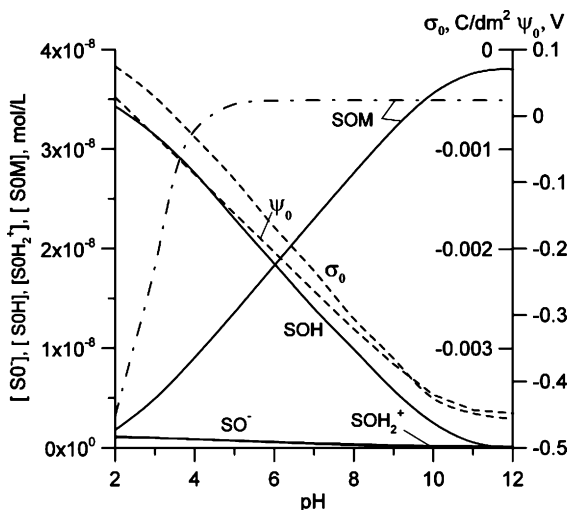
$$-\sigma_s = \sigma_d = -(8\epsilon\epsilon_0 RT)^{1/2} \sinh(F\psi_d/2RT),\tag{27.33}$$

where ϵ is the relative (specific) permittivity of solution; ϵ_0 is the permittivity of vacuum [$8.85 \cdot 10^{-13} \text{ C}^2(\text{J dm})^{-1} = 8.85 \cdot 10^{-13} \text{ F dm}^{-1}$]; I is the ionic strength of solution (mol dm^{-3}).

Thus, we have a closed system of equations, which in the general case can be solved by an iteration method with respect to component concentrations in liquid phase and in adsorbed state, as well as density charges, σ , and potentials, ψ , of specified planes.

An example of such solution for the system including components M^+ , A^- , H , SOH , SOH_2^+ , SO^- , $\text{SO} \cdot \text{M}$ and $\text{SOH}_2 \cdot \text{A}$, is plotted in Fig. 27.2. The calculations

Fig. 27.2 The effect of pH on the physicochemical and electrostatic characteristics of the model system



were carried out for a colloidal system with particle concentration of 10 mg dm^{-3} . When calculating its molar concentration, we assumed that the sorption site density is $N_S = 2.31 \text{ sites/nm}^2$ ($2.31 \cdot 10^{16} \text{ sites/dm}^2$), whence $N_{SA} = N_S/N_A = 3.837 \cdot 10^{-8} \text{ mol dm}^{-2}$ (Wang et al. 2001; Goldberg 2002). For the specific surface of particles $S_A = 1 \text{ m}^2 \text{ g}^{-1}$ ($10^5 \text{ dm}^2 \text{ kg}^{-1}$), from formula Eq. 27.19, we have $[\text{SOH}]^T = 3.837 \cdot 10^{-8} \text{ mol dm}^{-3}$. Next, it was assumed that $C_1 = 1.0 \cdot 10^{-2}$, $C_2 = 0.1 \cdot 10^{-2} \text{ F dm}^{-2}$, $I = 0.0001 \text{ mol dm}^{-3}$. The logarithms of equilibrium constants: $\ln K_{\text{SOH}_2} = 1.0$, $\ln K_{\text{SO}} = -4.0$, $\ln K_{\text{SOM}} = 6.0$, $\ln K_{\text{SOH}_2A} = -5$. The concentrations of M^+ and A^- ions were taken equal to $10^{-9} \text{ mol dm}^{-3}$.

The calculations (Fig. 27.2) showed, in particular, the high sensitivity of adsorption of metal ion on the exchange complex to variations in pH. Interestingly, the plots $[\text{SOM}] = f[\text{pH}]$ differ from analogous plots (dash-and-dot line) calculated with the assumption that the role of electrostatic interactions is negligible. It can also be seen that the magnitudes of negative charge and potential on o -plane increase with increasing pH.

27.2 On Modeling Approach for Multicomponent Solute Transport

Coupled convective–diffusive transport of multicomponent solutes including colloid particles in porous media is studied using a numerical technique based on LEHGC code (Yeh et al. 1995). The Lagrangian-Eulerian Model used in the HydroGeo-Chemical code, LEHGC, is the state of the art coupled-transport code. LEHGC solves a set of two-dimensional, partial differential equations describing transport with a hybrid Lagrangian-Eulerian finite-element method. LEHGC solves a

system of transport and geochemical equilibrium equations that are divided into two subsystems, which are solved in an iterative fashion. LEHGC is a FORTRAN code with a reasonable level of documentation and a test history. In particular, LEHGC can be used to enhance our understanding of the fate and transport of radioactive contaminants in the presence of colloids. LEHGC provides for multiple surface complexation and ion exchange sites.

27.2.1 Tests and Illustrative Examples

The solution of migration problem implies the hydrochemical and hydrodynamic description of the system.

27.2.1.1 Hydrogeochemical Characteristic of the System

Consider the migration of a univalent cation M^+ , able to enter in reactions of surface complex formation (27.22) with colloidal particles that have active hydroxyl sites $SiOH$. The presence of ion OH^- enables the formation of a neutral complex MOH^0 , which is considered as a nonsorbable component. Suppose also that ion M^+ is adsorbed according to the same scheme (27.22) on a solid/mineral phase containing hydroxyl groups SOH . The reactions of protonation and deprotonation of surface complexes follow Eqs. 27.20 and 27.21. We suppose that the solution is represented by a background electrolyte of a univalent salt KA (K^+ is a cation, A^- is an anion).

This type of reaction corresponds to the matrix of stoichiometric coefficients in Table 27.1. Symbols $Bo_{o,\beta}^{m,i}$ show virtual electrostatic components (*Boltzmann* particles), formed by the electric planes o and β of movable colloids (m) and the immobile mineral phase (i). The table gives the constants of appropriate equilibria for the basic calculation variant.

The initial and boundary concentrations of components are described by the values given in Table 27.2 (basic calculation variant). Rock density is $\rho_b = 2.2 \text{ kg/dm}^3$. The electrostatic interactions are determined by the capacity characteristics of potential layers $C_o^{m,i}$ and $C_\beta^{m,i}$, as well as the phase surface per unit weight $S_A^{m,i}$ (indices m and i refer to colloids and solid phase, Table 27.3).

In all calculations hydrogen ion, H^+ , was considered as a migrating component, i.e., the concentrations of $[H^+]$ are not fixed, but calculated in the solution of the transport problem.

27.2.1.2 Hydrodynamic Model Parameters

Test variants deal with one-dimensional (in x direction) migration of a multicomponent solution in a porous medium ($\phi = 0.2$) with a length of 1 m (simulation of experiment in a filtration column). The Darcy velocity $q = 0.01 \text{ m/d}$

Table 27.1 Matrix of stoichiometric coefficients and equilibrium constants (for the basic variant)

	M ⁺	K ⁺	A ⁻	H ⁺	SiOH	Bo _o ^m	Bo _β ^m	SOH	Bo _o ⁱ	Bo _β ⁱ	log(<i>K</i>)
M ⁺	1	0	0	0	0	0	0	0	0	0	—
K ⁺	0	1	0	0	0	0	0	0	0	0	—
A ⁻	0	0	1	0	0	0	0	0	0	0	—
OH ⁻	0	0	0	-1	0	0	0	0	0	0	-13.98 ^a
MOH ⁰	1	0	0	-1	0	0	0	0	0	0	-2.0 ^b
MA ⁰	1	0	1	0	0	0	0	0	0	0	1.0 ^c
SiO ⁻	0	0	0	-1	1	-1	0	0	0	0	-8.5 ^d
SiOH ₂ ⁺	0	0	0	1	1	1	0	0	0	0	1.5 ^e
SiOM	1	0	0	-1	1	-1	1	0	0	0	4.0 ^f
SO ⁻	0	0	0	-1	0	0	0	1	-1	0	-8.5 ^g
SOH ₂ ⁺	0	0	0	1	0	0	0	1	1	0	1.5 ^h
SOM	1	0	0	-1	0	0	0	1	-1	1	6.0 ⁱ

^a—(pH + pOH)

^b*K*_{MOH}

^c*K*_{MA}

^d*K*_{SiO}

^e*K*_{SiOH₂}

^f*K*_{SOH}

^g*K*_{SO}

^h*K*_{SOH₂}

ⁱ*K*_{SOH}.

Table 27.2 Initial and boundary total concentrations of components

Concentrations, mole/dm ³	M ⁺	K ⁺	A ⁻	pH	SiOH	SOH
Initial (t = 0, x > 0)	1 · 10 ⁻¹²	1 · 10 ⁻²	1 · 10 ⁻²	7.0	1 · 10 ⁻¹¹	1 · 10 ⁻⁸
Boundary (t > 0, x = 0)	1 · 10 ⁻¹⁰	1 · 10 ⁻¹	1 · 10 ⁻¹	7.0	1 · 10 ⁻⁶	1 · 10 ⁻⁸

Table 27.3 Parameters for calculating electrostatic interactions

Parameters	<i>C</i> _o ^m	<i>C</i> _β ^m	<i>S</i> _A ^m	<i>C</i> _o ⁱ	<i>C</i> _β ⁱ	<i>S</i> _A ⁱ
Values	1 · 10 ⁻²	0.1 · 10 ⁻²	5 · 10 ⁷	1 · 10 ⁻²	0.1 · 10 ⁻²	1 · 10 ¹
Dimensions	Fdm ⁻²	Fdm ⁻²	dm ² kg ⁻¹	Fdm ⁻²	Fdm ⁻²	dm ² kg ⁻¹

(4.17 · 10⁻³ dm/h), the longitudinal dispersion coefficient $D_L = 10^{-4}$ m²/d (4.17 · 10⁻⁴ dm²/h), the calculation time is 12 d. Within this time, the front of inert component covers the major portion of the distance between the inlet and outlet boundaries of the model domain. The parameters of the spatial and temporal fragmentation are as follows: Δx = 0.05 m (200 model blocks), Δt = 0.1667 d (4 h). The concentrations of all components, including colloids, at the inlet boundary of the model domain was taken to be constant.

27.2.2 Sample Problems and Analysis of Migration Process

Consider two samples, demonstrating the significance of the physicochemical interactions involving the colloidal fraction for the formation of migration fluxes.

Sample 1 illustrates the effect of pH on the displacement velocity of the front of total concentration of M^+ ion with the assumption that the role of its colloidal transport is negligible (K_{SOM} , K_{SO} , and $K_{SOH_2} < 10^{-10}$) (Fig. 27.3). With $pH > 4$, when the value of $K_{MOH} = 10^{-2}$ (the full lines in the plot in Fig. 27.3), the concentration of hydrogen ions is not sufficient for their competition with M^+ ions for adsorption sites to be of any significance. Conversely, a decrease in pH to a value equal to unit, makes the adsorption of M^+ ions practically impossible, with the result that these ions start migrating with the velocity of water particles (inert component).

It is worth mentioning that in the case under consideration ($K_{MOH} = 10^{-2}$), even when the values of pH are high (>4), the migration velocity of M^+ ion remains high (during the calculation time $t = 12$ d, the front of this ion covers a distance of about 1/3 of the length of the model domain). This can be attributed to the formation in solution of MOH^0 complex, which, in this problem formulation, is assumed not to be adsorbed by rock. To prove the validity of this assumption, we carried out calculations at very low values of the constant $K_{MOH} (=10^{-6})$. It can be seen (Fig. 27.3, dashed lines in the plot) that, with the exclusion from consideration of MOH^0 ions, which almost do not form at K_{MOH} values as low as that, results in an abrupt increase in the adsorption of M^+ ion on the rock in the entire range of $pH > 2$

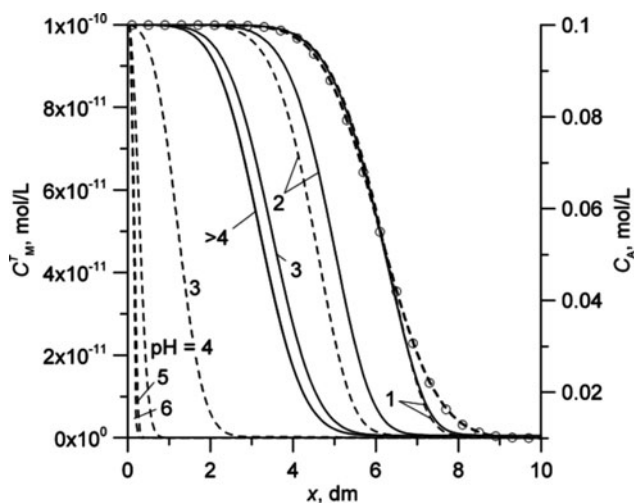


Fig. 27.3 The effect of pH of the boundary solution on the distribution of total concentration of component M in the flow. The *full curves* are for $K_{MOH} = 10^{-2}$, the *thin dashed lines* are for $K_{MOH} = 10^{-6}$. The adsorption of M^+ ion by colloids was neglected in the calculations. Hereafter, the *thick dashes* show the concentration distribution of anion A^- (the right axis of the plot), *dots* are for an analytical solution for an inert component

as compared with the basic variant $K_{\text{MOH}} = 10^{-2}$. Thus, calculations with $\text{pH} = 6$ have shown (Fig. 27.3) that almost all the dissolved component was adsorbed near the inlet boundary of the flow (in the domain $x < 0.1$ dm).

This and the following figures (Figs. 27.3–27.7) give functions $A^- = f(x)$, which characterize the migration of the front of an inert component (anion A^-). The appropriate distributions were obtained by numerical and analytical methods (the fundamental solution of the boundary value problem). The practically coinciding curves demonstrates the high accuracy of the numerical algorithm of solving transport equations used in the software package LEHGC.

Sample 2 gives an insight into the effect of adsorption of M^+ ion of the aquifer material during the migration of solution containing colloidal particles, which also can adsorb this ion (Fig. 27.4). It can be easily seen that an increase in the constant of adsorption on colloids increases the displacement velocity of the migration front.

In all examples of calculations, the front moves with the same velocity as water particles at $K_{\text{SiOM}} = K_{\text{SOM}} = 10^{+6}$. The degree of influence of the constant K_{SiOH} in the range $K_{\text{SiOM}} < K_{\text{SOM}}$ depends, on the one hand, on solution pH and, on the other hand, on the ability of ion M^+ to form the hydroxyl form MOH^0 . Thus, the calculations show that a decrease in solution pH is a factor facilitating the acceleration of concentration front migration, also because of the competition between H^+ and M^+ ions. In a near-neutral solution, ion M^+ is retained in solution also due to complexation with hydroxyl group (Fig. 27.4a); therefore, a drop in the equilibrium constant K_{MOH} by several orders leads to an abrupt increase in adsorption and, accordingly, to a very large decrease in mass transport velocity. Such dramatic effect was not observed during the migration of acid solutions (Fig. 27.4b), since the high concentrations of H^+ ions hamper the adsorption of M^+ ion even at low values of K_{MOH} constant.

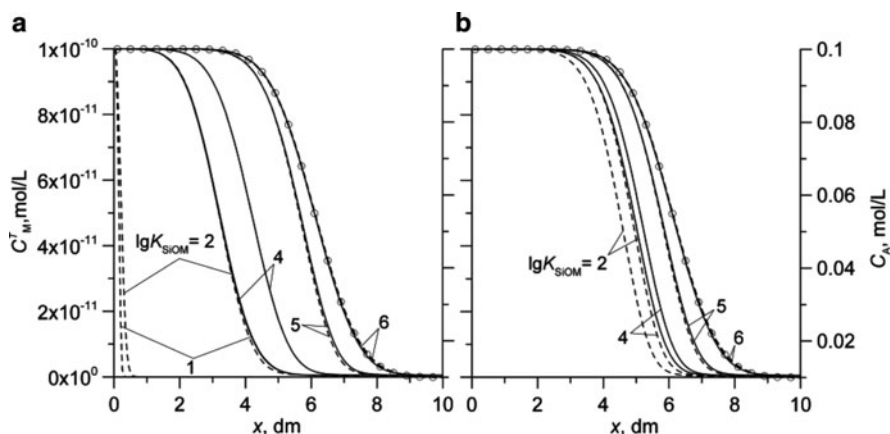


Fig. 27.4 The solution of the migration problem of component M, being adsorbed by sediment, in a solution containing active colloidal particles. (a) pH 7, (b) pH 2. The full and dashed curves are the results of calculations made at $K_{\text{MOH}} = 10^{-2}$ and 10^{-6} , respectively. The plots reflect the effect of the values of constant K_{SiOM} on concentration distributions

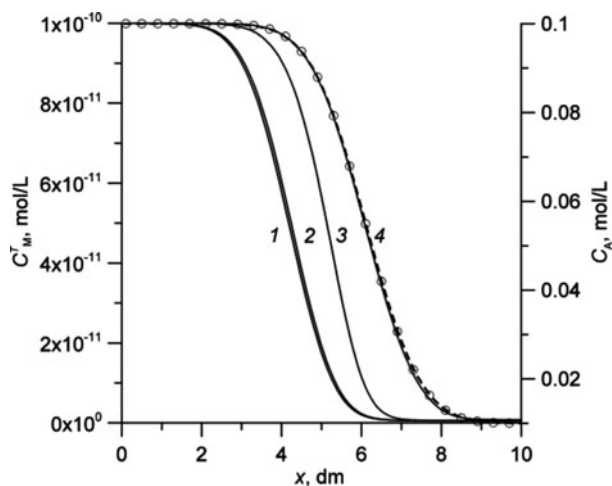


Fig. 27.5 The effect of the electric capacity of potential layers on the character of plots of total concentration of the component M. $C_M^T = C_M + C_{M\text{Coll}}$, C_M is the concentration in liquid phase, $C_{M\text{Coll}}$ is the concentration on colloids. (1) $C_o^m = C_o^i = 1 \cdot 10^{-2}$, $C_\beta^m = C_\beta^i = 0.1 \cdot 10^{-2} \text{ F/dm}^2$; (2) $C_o^m = C_o^i = 1 \cdot 10^{-4}$, $C_\beta^m = C_\beta^i = 0.1 \cdot 10^{-4} \text{ F/dm}^2$; (3) $C_o^m = C_o^i = 1 \cdot 10^{-6}$, $C_\beta^m = C_\beta^i = 0.1 \cdot 10^{-6}$; (4) $C_o^m = C_o^i = 1 \cdot 10^{-8}$, $C_\beta^m = C_\beta^i = 0.1 \cdot 10^{-8} \text{ F/dm}^2$. The calculations were carried out for the basic variant at pH 7, $K_{\text{SiOM}} = 4$, $K_{\text{SOM}} = 6$

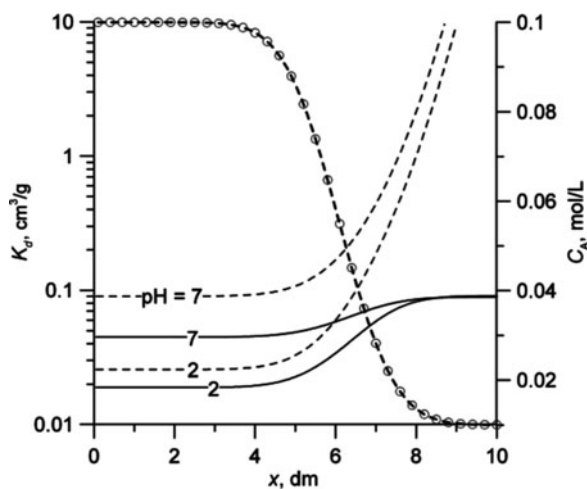


Fig. 27.6 Calculated values of the effective constant of sorption distribution K_d . The *full curves* are for $K_{\text{MOH}} = 10^{-2}$, the *dashed curves* are for $K_{\text{MOH}} = 10^{-6}$

Finally, a decrease in the electric capacity of potential layers $C_o^{m,i}$ and $C_\beta^{m,i}$, facilitating the enhancement of adsorption interactions, also cause an increase in the migration velocity of the adsorbed component (Fig. 27.5).

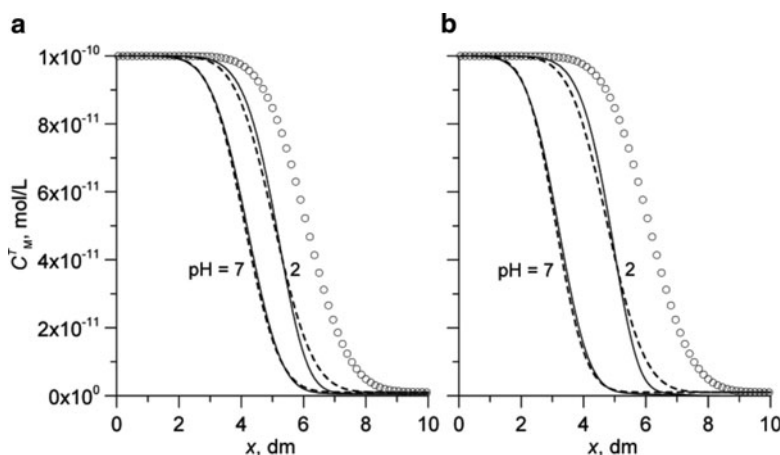


Fig. 27.7 The comparison of model curves for the function C_M^T (full lines) with analytical solutions of the fundamental problem (dashed curves) obtained at different values of the retardation factor, R . (a) $K_{MOH} = 10^{-2}$, (b) $K_{MOH} = 10^{-6}$. Other conventional notations see in Fig. 27.6 and the text description

The effect of changes in the hydrochemical characteristics of the system on the calculated value of the sorption distribution coefficient $K_d = [M]_{ADS}/[M]^T$ ($[M]_{ADS}$ is the concentration of the component on active sites of the rock, kg/kg, $[M]^T$ is the total concentration of the component in solution, kg/dm³) is illustrated by the plot in Fig. 27.6. In the boundary domain of weak variations in concentration functions, we have $K_d = 0.045$ dm³/kg (pH 7, $K_{MOH} = 10^{-2}$), $K_d = 0.019$ dm³/kg (pH 2, $K_{MOH} = 10^{-2}$), $K_d = 0.09$ dm³/kg (pH 7, $K_{MOH} = 10^{-6}$) and $K_d = 0.026$ dm³/kg (pH 2, $K_{MOH} = 10^{-6}$).

With these values, the estimates of effective retardation factor $R = 1 + K_d \rho_b / \phi$ ($\rho_b = 2.2$ kg/dm³; $R = 1.5, 1.21, 1.99, 1.29$) almost exactly determine the position of concentration fronts calculated from the fundamental solution of the appropriate boundary problem (Fig. 27.7). This means that the analysis of an equilibrium system for static conditions, allowing one to obtain calculated values of K_d , can be an effective instrument for subsequent migration calculations.

27.3 A Conceptual Model for the Subsurface Transport of Plutonium on Colloidal Particles Involving Surface Complexation Reactions

27.3.1 The Basic Chemistry of Plutonium

Plutonium belongs to the group of elements-actinides, including 14 elements with atomic numbers between 90 and 103. The atomic number of plutonium is 94.

Variations in the atomic weights of plutonium determine the isotopic series from Pu-232 to Pu-246. Practically all plutonium isotopes are α -emitters. The half-life varies from 1 min to more than 1,000 years. The values of $t_{1/2}$ (years) for most stable plutonium isotopes are as follows: 87.8 for ^{238}Pu , $2.41 \cdot 10^4$ for ^{239}Pu , $6.54 \cdot 10^3$ for ^{240}Pu , and 14.4 for ^{241}Pu (beta-decay mode). Important isotopes with respect to dose calculations include ^{239}Pu , ^{242}Pu , and ^{238}Pu .

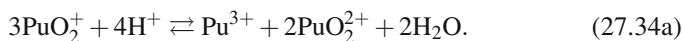
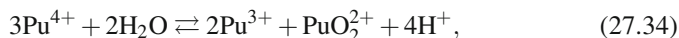
Plutonium is essentially an anthropogenic radionuclide that is produced in nuclear reactors from naturally occurring radionuclides by neutron capture. Plutonium is a component of practically all types of radioactive wastes that form during nuclear reactions. The appearance of plutonium in the environment is also due to nuclear weapon tests. According to different estimates, from 3 to 4 t of plutonium was released into the environment in the period of nuclear surface tests. Earth surface pollution (in Belarus, Ukraine, Russia, and some other European countries) by plutonium isotopes (Pu-238, Pu-239, and Pu-240) was also caused by the Chernobyl accident on April 26, 1986. Data on the total mass of the released plutonium is controversial; in the opinion of some experts, it can reach 15 kg. Despite the very long half-lives of some of the most important isotopes of Pu, the radioactivity per unit of weight (the “specific activity”) for these radionuclides is high enough for tiny quantities of the material to be dangerous (Fioravanti and Makhijani 1997).

The chemistry of plutonium is more complex than that of any other actinide. In the following analysis, we will generally review the specific features of the chemical behavior of Pu in the subsurface environment.

27.3.1.1 Oxidation States of Plutonium

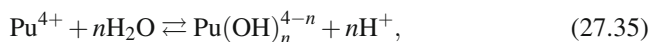
One of the most important parameters that control the geochemical features of plutonium behavior in the subsurface hydrosphere is its oxidation state. This state is determined by the origin of the element and way of its release from the pollution sources, as well as a large number of physicochemical parameters characterizing the migration conditions of Pu in the aeration zone and in aquifers. Under typical environmental conditions, plutonium is known to exist in four different oxidation states, Pu(III), Pu(IV), Pu(V), and Pu(VI), and thermodynamic calculations admit the co-existence of different states in the same solution (Katz et al. 1986). Each such state determines a different degree of involvement of Pu^{3+} , Pu^{4+} , PuO_2^+ , and PuO_2^{2+} ions in the reactions of hydration, complex formation, precipitation–dissolution, and in sorption processes. The determination of the true oxidation state of Pu is a difficult experimental problem, which can be solved successfully in few laboratories. The true state of plutonium in water cannot be predicted by calculations based only on the measured oxidation-reduction potential (without regard for complex formation and other chemical reactions). Disproportionation reactions (in this case, auto-oxidation–auto-reduction) also have a considerable effect on this characteristic. In these reactions, plutonium behaves as an element that serves as both oxidizing and

reducing agent (Flury and Harsh 2003), for example, $\text{Pu(IV)} \rightleftharpoons \text{Pu(III)} + \text{Pu(VI)}$ and $\text{Pu(V)} \rightleftharpoons \text{Pu(III)} + \text{Pu(VI)}$, or, in the explicit form,



A prerequisite for disproportionation is the similarity of the oxidation potentials of appropriate ionic pairs. Appreciable disproportionation of Pu(IV) takes place in HClO_4 and HNO_3 solutions with concentrations below 1 mol/L where it accelerates with decreasing pH. The introduction of anions that form complexes with actinides, in particular, with Pu(IV), Pu(V), and Pu(VI), accelerates the disproportionation process.

In groundwater systems with low TDS, under oxidation conditions, when Eh is in the range between ~ 0 and $\sim +600$, and near-neutral acid-alkaline conditions, when pH is in the range between around 6 and 8, plutonium exists in IV and V oxidation state (Fig. 27.8a). Choppin and Morgenstern (2001) reported that “in most natural systems” plutonium is found in the IV and V oxidation states. In aqueous solutions, Pu(IV) ions, having high positive charge, are easily hydrolyzed, forming hydro complexes, Pu(OH)_n^{4-n} ($n = 1, 2, 3, 4$),



here, the partial thermodynamic equilibrium constants are (Guillaumont et al. 2003) $\log K_1^0 = (0.6 \pm 0.2)$, $\log K_2^0 = (0.6 \pm 0.3)$, $\log K_3^0 = -(2.3 \pm 0.4)$, $\log K_4^0 = -(8.5 \pm 0.5)$. From the viewpoint of formal thermodynamics, Pu(IV) in such

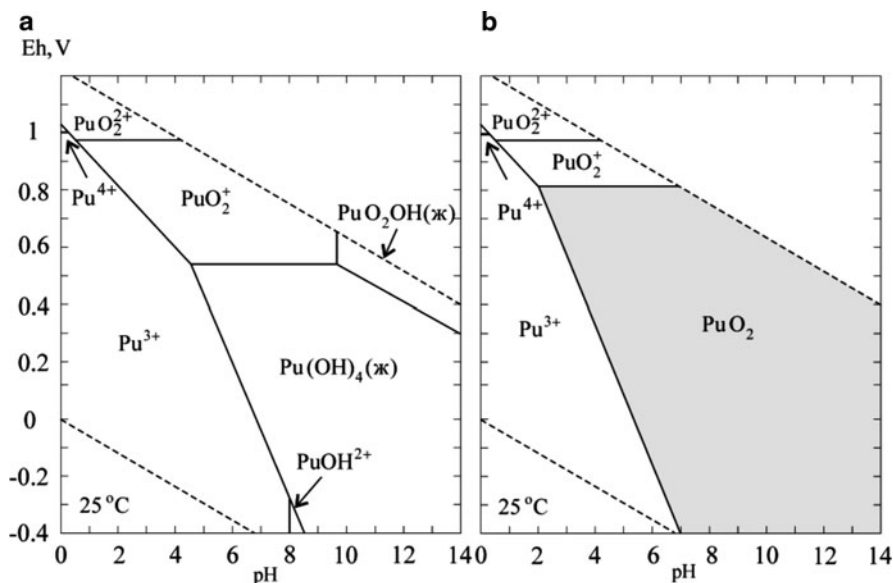


Fig. 27.8 Eh-pH diagrams (Flury and Harsh 2003). (a) Dissolved forms of actinides; (b) plutonium ions with different oxidation degrees in thermodynamic equilibrium with $\text{PuO}_2(\text{cr})$

systems should have very low migration capacity because of both the high sorption by rock and the low solubility of solid (crystalline and amorphous) phases of $\text{PuO}_{2(\text{cr, am})}$ and $\text{Pu}(\text{OH})_{4(\text{cr, am})}$ in equilibrium with solution (Fig. 27.8b).

In other hydrogeochemical systems with acid–alkaline and redox conditions differing from those mentioned above, plutonium may have oxidation states of III, V, and VI (Fig. 27.8). Under reducing conditions, the III and IV oxidation states would be the most stable with the III state dominating at pH values below 8.5 and IV state dominating at pH values above 8.5 (Smith and Amonette 2006).

Thus, estimates for the WIPP (Waste Isolation Pilot Plant) site, a deep geological repository licensed to permanently dispose of transuranic radioactive waste, New Mexico, USA, showed the prevailing oxidation state of plutonium in the chloride brine to be VI (Runde 2000). Moreover, chloride complexes of $\text{Pu}(\text{VI})$ will be more stable than chloride complexes that are formed with $\text{Pu}(\text{IV})$ and $\text{Pu}(\text{V})$.

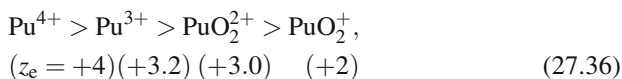
According to preliminary estimates, the oxidation state of plutonium $\text{Pu}(\text{IV})$ dominates (up to 100%) in liquid RW utilized by injection into deep horizons in the Deep-Well RW Disposal Site at Siberian Chemical Plant (see Sects. 3.3.4 and 23.1). Within the plume of radioactive groundwater pollution due to leaks from Lake Karachai (see Sects. 15.3 and 23.3), plutonium occurs in two dominating oxidation states – $\text{Pu}(\text{IV})$ and $\text{Pu}(\text{V})$, in nearly equal concentrations (40–50%); the state $\text{Pu}(\text{VI})$ can also be met in up to 10% of the total plutonium concentration in polluted waters.

Notwithstanding the large charge of the cation and the low values of the solubility product of plutonium salts, such as PuO_2 and $\text{Pu}(\text{OH})_4$, there exist factors that inhibit the sorption and precipitation of this actinide. These factors are associated with the formation in solutions of complexes with inorganic (such as F , CO_3 , PO_4 , SO_4) and organic ligands. The process of polymerization of ions in solutions, which will be considered below, acts in the same direction.

27.3.1.2 Hydrolysis and Polymerization of Pu

The polymerization reactions are very closely related with and proceed parallel to multi-stage hydrolysis reactions. Therefore, these processes are difficult to study separately. Plutonium polymerization in aqueous solutions is among the key factors that affect the evaluation of thermodynamic constants and the accuracy of calculating the dissolved forms.

The hydrolysis and polymerization capacity of plutonium in different oxidation states is the higher, the greater is the effective charge of the central ion (z_e), as is reflected in the following series (Clark 2000):

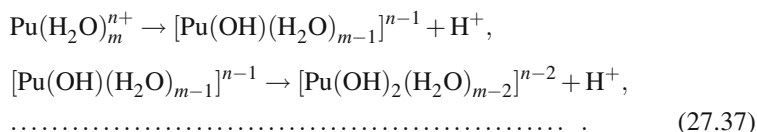


i.e., the maximal degree of plutonium polymerization should be expected in the solutions where it is in the state $\text{Pu}(\text{IV})$. Since this degree of plutonium oxidation

prevails over others in natural–anthropogenic hydrogeochemical systems, the further analysis can be reasonably limited to reactions involving the original cation Pu^{4+} .

The large charge of Pu(IV) allows it to readily hydrolyze and form a large number of particles at once, even at low pH. Taking active part in hydrolysis, Pu(IV) can form stable intrinsic colloids with concentrations above 10^{-6} M, even in diluted acid solutions (Runde 2000).

A chain of hydrolysis reactions can be written with the incorporation of water molecules that hydrate Pu^{4+} cation (Johnson and Toth 1978):



Formally, the reactions look like conversion of ligands of H_2O into OH in each compound.

The molecular mass of polymer molecules may vary from $4 \cdot 10^3$ to $1 \cdot 10^{10}$. The size of colloidal particles also varies within a wide range (from 1 nm to 1 μm). In the general case, the degree of polymerization depends also on plutonium concentration. The rate of polymerization increases with increasing temperature. The density of colloidal particles approaches the density of crystalline PuO_2 oxide. Depolymerization is very slow in most cases (The chemistry of the actinide elements 1986). X-ray–adsorption structural studies confirmed the conclusion that the colloidal hydroxopolymer particles of Pu(IV) have structural characteristics typical of PuO_2 (Runde 2000). At the same time, each colloidal particle includes many functional groups and can be considered as an amorphous oxyhydroxy-component.

The formation of intrinsic Pu(IV) colloids, along with the disproportionation reactions, is among the key processes that hamper the evaluation of thermodynamic constants (in particular, the solubility product of the forming compounds) and reduce the reliability of predicting the behavior of this actinide in natural waters. The formation of intrinsic colloids, as well as complex formation reactions, increases the solubility of the equilibrium solid phase – PuO_2 or $\text{Pu}(\text{OH})_4$.

The sorption properties of colloidal plutonium should be expected to differ from such for plutonium in simple ionic forms. Though Pu(IV) colloids are believed to be stable formations, they can precipitate from solution because of changes in its ionic composition, ionic strength, and pH. For example, the degree of polymerization was found to increase with decreasing HNO_3 concentration (Zhao and Steward 1997): this degree increases from zero at HNO_3 concentration of 0.1 M HNO_3 to 100% at 0.04 M HNO_3 .

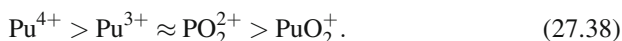
Overall, the formation of intrinsic colloids can be regarded as a factor intensifying the transport of this radionuclide in groundwater at least when in low concentration, as was confirmed primarily by laboratory experiments in filtration columns (Flury and Harsh 2003). Moreover, from the viewpoint of subsequent migration considerations, it is important to note that intrinsic colloids can be adsorbed

on mineral colloidal particles, resulting in the formation of pseudocolloids with a complex structure, which are also able to migrate with velocities higher than those of the ionic forms of occurrence of this actinide in solution.

27.3.1.3 Complexation

Plutonium is known to form a number of complexes with the majority of principal anions in natural waters (hydroxyl, $\text{HCO}_3^-/\text{CO}_2^{2-}$, Cl^- , SO_4^{2-} , PO_4^{3-} , NO_3^- , F^-), as well as to form organic-metal complexes. The presence of these complexing agents in the environment can also alter the oxidation state of plutonium and thus can have multiple impacts on its mobility (Smith and Amonette 2006). Thus, complexation reactions between Pu and principal anions tend to decrease its sorption, and organic materials can reduce Pu from higher to lower oxidation states. When pH is low (i.e., below about five or six), and when there are high concentrations of dissolved organic carbon, it appears that plutonium–organic complexes may control the sorption and mobility of plutonium in the environment (EPA 1999; Smith and Amonette 2006).

The values of complex-formation constants depend on the degree of plutonium oxidation and vary within a wide range (Guillaumont et al. 2003). Overall, the stability of complexes with anions are higher with Pu(IV) as compared with Pu(III), Pu(V), and Pu(VI), such that the ability of plutonium to form complexes decreases in the following series (Katz et al. 1986):



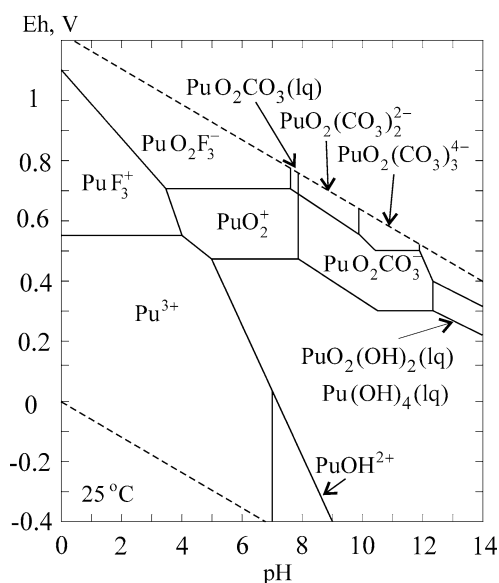
At pH values above 7, the mobility of plutonium can be influenced by the concentrations of dissolved carbonate and hydroxyl ions and the fact that the hydroxy-carbonate mixed ligand complexes are among the strongest complexes of plutonium known to exist in the environment (EPA 1999). In the decreasing order of stability of their complexes, the anions form the following series:



This series suggests that plutonium would be most mobile in high-pH carbonate-rich groundwaters. Fluoride complexes can also play an important role in the formation of mobile migration forms of plutonium, especially, Pu(IV) and Pu(VI).

This conclusion is illustrated by a Eh–pH diagram in Fig. 27.9, showing the thermodynamic stability areas of different Pu species. The diagram is calculated for groundwater from well J-13 drilled within the proposed Yucca Mountain Nuclear Waste Repository site, Nevada, USA. Water from well J-13 is a reference water for the unsaturated zone near the proposed emplacement area. J-13 water is fairly low in ionic strength (about 3.7 mmol), with carbonate (about 2.8 mmol) and hydroxide as predominant potential ligands (Callahan et al. 2000; Flury and Harsh 2003; Reimus et al. 2007). Potassium is a dominant cation. Similar results were obtained from thermodynamic calculations given in another work (Runde 2000).

Fig. 27.9 Eh-pH phase diagram for plutonium in water containing carbonate, fluoride ions, and hydroxyl groups (Flury and Harsh 2003). Plutonium concentration 10^{-5} M, the activities of ions $[\text{HCO}_3^-] = 10^{-2.63}$, $[\text{F}^-] = 10^{-3.96}$, and $[\text{SiO}_2] = 10^{-3.3}$. The dashed lines are the upper and lower boundaries of water stability field



It can be easily seen that in near-neutral water, with pH close to 7 and Eh varying from 0 to $+(300\text{--}450)$ mV, plutonium occurs in the oxidation state IV (migration form of $\text{Pu}(\text{OH})_4$). The shift into the domain of strongly oxidized waters ($\text{Eh} > 450$ mV) facilitates plutonium conversion into oxidation states V and VI with the predominance of carbonate complexes and the ionic form of PuO_2^+ . The oxidation state of plutonium III (Pu^{3+} ion is predominant) in solutions with $\text{pH} > 5\text{--}6$ is typical only of strong reduction conditions (Fig. 27.8a).

Finally, the presence of organic acids, which often are components of radioactive solutions or determine the natural hydrogeochemical background, can also influence the solubility of plutonium compounds, enhancing its migration capacity in rocks.

27.3.1.4 Sorption Data Analysis

The oxidation-reduction potential, water solution pH, and the concentration of carbonates and NOM, have the greatest effect on the degree of Pu sorption. The measured values of K_d for plutonium have shown a wide range “from low to extremely high affinities” (EPA 1999). The typical values range from $11\text{ cm}^3/\text{g}$ to as much as $300,000\text{ cm}^3/\text{g}$ (Smith and Amonette 2006). Interactions of Pu-containing solutions with natural organic matter and hydroxides of Fe and Mn contained in the porous matrix can cause changes in the oxidation state of Pu through redox transformations in the process of subsurface solute migration from the oxidation state Pu(V, VI) to the oxidation state Pu(IV), and vice versa. Other conditions being the same, Pu(VI) and Pu(V) feature lower sorption (Silva and Nitsche 1995). Thus, the

coefficient of sorption distribution (K_d) was found to drop by an order of magnitude (from $K_d^{\text{Pu(IV)}} = 2,100$ to $K_d^{\text{Pu(VI)}} = 250 \text{ cm}^3/\text{g}$) with the change in plutonium oxidation state from Pu(IV) to Pu(VI) (Kaplan and Wilhite 2000).

Thus, the passage of plutonium from the state Pu(IV) to the state Pu(VI) is the least favorable factor from the viewpoint of conservative forecasts. The possibility of conversions of this type was mentioned by Kaplan and Wilhite (2000), who give a reference to appropriate field materials. The same study draws attention to the difference between the values of K_d , obtained in laboratory experiments (K_d^L) and those derived from the interpretation of field observation data on the ratio between plutonium concentration in pore solution and on the mineral matrix of core material (K_d^F): $K_d^L \ll K_d^F$. Such ratio can be attributed to (1) the role of diffusion penetration of plutonium into rock matrix, especially into fringes of hydroxides and oxides of iron and aluminum, which coat mineral grains and (2) the passage of plutonium from the oxidation state Pu(VI) into the state Pu(IV), again because of the iron oxides and hydroxides, which have a kind of catalytic effect.

The above circumstances, in particular, make it very difficult to experimentally study the parameters of sorption interaction between plutonium and mineral phase – the rock and colloidal particles, represented by aluminosilicates and metal hydroxides and oxides. Therefore, for expert estimates in the absence of experimental data on the sorption of plutonium in certain oxidation state or when experimental studies are limited for technical reasons, one can be recommended to use experimental parameter estimates obtained for other actinides that are geochemical analogues of plutonium. Thus, an analogue for Pu(IV) can be Th(IV), and that for Pu(VI) can be U(VI).

As it was repeatedly noted, a substantial body of experimental material has been accumulated to characterize the sorption of actinides, in particular, plutonium, on sediment and colloidal particles under various geochemical conditions. Leading laboratories, primarily, in Western Europe and USA, were deeply involved in such studies, aimed to substantiate the construction of repositories of RW and spent nuclear fuel, as well as to assess the risk of operation of existing facilities in nuclear-industry and power complexes (Cantrell and Riley 2008). In this context, we give the results of some studies of sorption.

Thus, an experimental series was carried out to study the sorption of Pu(V) on colloids represented by several mineral formations: montmorillonite, hematite, silicon earth, and smectite (Lu et al. 1998a, 2003). The liquid phase was represented by water from well J-13 in the zone of potential influence of Yucca Mountain repository for HLW and spent nuclear fuel disposal. One of approaches to the interpretation of experiments was based on a kinetic model of heterogeneous sorption sites (Painter et al. 2002; Wittman et al. 2005). Data on the total (over sites of different types) equilibrium adsorption on colloids are given in Table 27.4 (Wittman et al. 2005). As can be seen from this table, hematite shows higher sorption capacity, while that of silicon earth and montmorillonite is lower.

About the same range of variations in the coefficient of sorption distribution was obtained from an alternative interpretation (Painter et al. 2002): $K_d = 1.1 \cdot 10^3 - 7.6 \cdot 10^4 \text{ cm}^3/\text{g}$. Hysteresis of sorption process was observed in both works, manifesting

Table 27.4 Plutonium distribution coefficients (J-13 water)

Mineral	K_d , cm ³ /g
Silica (SiO ₂)	$2.4 \cdot 10^{3b} - 3.3 \cdot 10^{4a}$
Hematite (α -Fe ₂ O ₃)	$1.3 \cdot 10^{5a}$
Montmorillonite	$8.2 \cdot 10^{3a}$
Smectite	$1.4 \cdot 10^{4b}$

^aColloid concentration is 200 mg/L^bThe same for 1,000 mg/L the mean diameter of colloidal particles is about 100 nm**Table 27.5** Plutonium desorption from the surface of colloidal particles after their exposure in J-13 water during 150 days

Mineral	Desorption, %	
	Pu(IV)	Pu(V)
Hematite (α -Fe ₂ O ₃)	0.0	0.01
Goethite (α -FeOOH)	0.57	0.77
Montmorillonite	8.23	0.48
Silicon earth (SiO ₂)	19.93	1.04

itself in a difference between the kinetic constants of sorption and desorption. Experimental studies also showed a difference between desorption kinetics of Pu(IV) and Pu(VI) from the surface of different minerals (Lu et al. 1998a). As can be seen from Table 27.5, Pu(IV) is desorbed more actively than Pu(V).

Another study (Lu et al. 1998b), devoted to examining Pu(IV) sorption in the form of *intrinsic* colloids or Pu(V) ions on colloids, represented by hematite and goethite, showed higher sorption rate of colloidal plutonium Pu(IV) as compared with “ionic” Pu(V). In this case, plutonium desorption in all variants featured kinetics much slower than that of sorption.

Some authors (Wang et al. 2001; Schwantes 2004) mention an approximate linear dependence of the rate characteristics of sorption interaction of actinides (as well as elements–analogues) on the values of their constant of the first stage of hydrolysis in aqueous solution (K_{MOH}). Following this logic and based on the previously published (Wang et al. 2001) and his own experimental results, Schwantes (2004) proposed a generalized formula

$$\log K \approx 2.32 \log K_{\text{MOH}} + 17.5, \quad (27.40)$$

which describes the sorption of plutonium, which is controlled by the constant, K , of reaction of surface complex formation similar to (27.4). Formula (27.40) with a confidence interval of $\pm 0.8 \log$ of unit makes it possible to evaluate the chemical equilibrium constant for a reaction involving plutonium in any of its four oxidation states (III, IV, V и VI). The sorbent is assumed to be the rock matrix with some “averaged” properties. With the use of this formula, one may try to obtain exact estimates of constant K or at least to gain a rough idea of the range of expected variations in K as a function of the oxidation state of plutonium, which is characterized by an individual value of K_{MOH} .

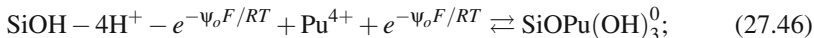
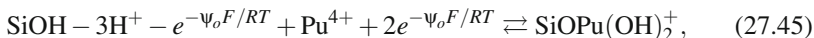
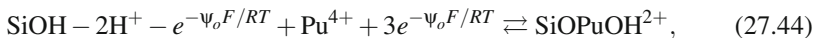
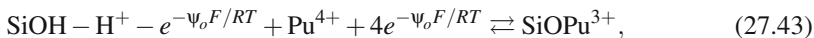
27.3.2 Examples of Modeling Assessments for Migration of the Sodium Nitrate Solution Containing Pu(IV) and Colloids

27.3.2.1 Problem Formulation

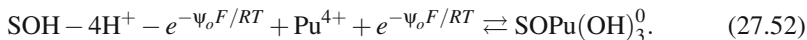
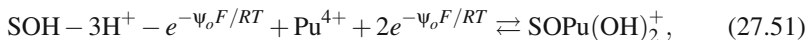
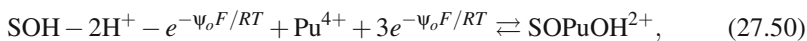
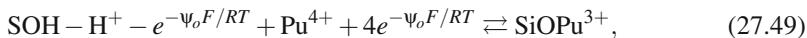
The problem formulation considered below corresponds best to simplified conditions of laboratory experiments, in which model radioactive solutions are prepared based on NaNO_3 salt. As before, we will consider one-dimensional migration in porous medium ($\phi = 0.2$) over a path of 10 dm. The Darcy velocity is $q = 0.01 \text{ m/d}$ ($4.17 \cdot 10^{-3} \text{ dm/h}$), the longitudinal dispersion coefficient is $D_L = 10^{-4} \text{ m}^2/\text{d}$ ($4.17 \cdot 10^{-4} \text{ dm}^2/\text{h}$), the calculation time is 11.263 d.

We consider the reactions of surface complex formation (Sect. 27.1) taking place

(a) on colloids:



(b) on the solid phase:



Complex formation reactions in liquid phase:

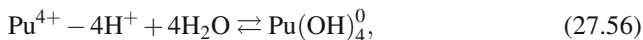
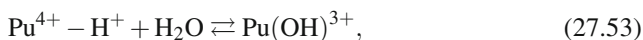


Table 27.6 Matrix of stoichiometric coefficients and equilibrium constants (for the base variant)

	Pu^{4+}	Na^+	NO_3^-	H^+	SiOH	Bo_o^m	Bo_β^m	SOH	Bo_o^i	Bo_β^i	$\log(K)$
Pu^{4+}	1	0	0	0	0	0	0	0	0	0	
Na^+	0	1	0	0	0	0	0	0	0	0	
NO_3^-	0	0	1	0	0	0	0	0	0	0	
OH^-	0	0	0	-1	0	0	0	0	0	0	-13.98
$\text{Pu}(\text{OH})^{3+}$	1	0	0	-1	0	0	0	0	0	0	0.6
$\text{Pu}(\text{OH})_2^{2+}$	1	0	0	-2	0	0	0	0	0	0	0.6
$\text{Pu}(\text{OH})_3^+$	1	0	0	-3	0	0	0	0	0	0	-2.3
$\text{Pu}(\text{OH})_4^0$	1	0	0	-4	0	0	0	0	0	0	-8.5
$\text{Pu}(\text{NO}_3)^{+3}$	1	0	1	0	0	0	0	0	0	0	1.95
SiO^-	0	0	0	-1	1	-1	0	0	0	0	-8.5
SiOH_2^+	0	0	0	1	1	1	0	0	0	0	1.5
SiOPu^{3+}	1	0	0	-1	1	-1	4	0	0	0	6.42
SiOPuOH^{2+}	1	0	0	-2	1	-1	3	0	0	0	1.7
$\text{SiOPu}(\text{OH})_2^+$	1	0	0	-3	1	-1	2	0	0	0	-8.5
$\text{SiOPu}(\text{OH})_3^0$	1	0	0	-4	1	-1	1	0	0	0	0.0
SO^-	0	0	0	-1	0	0	0	1	-1	0	-8.5
SOH_2^+	0	0	0	1	0	0	0	1	1	0	1.5
SOPu^{3+}	1	0	0	-1	0	0	0	1	-1	4	6.42
SOPuOH^{2+}	1	0	0	-2	0	0	0	1	-1	3	1.7
$\text{SOPu}(\text{OH})_2^+$	1	0	0	-3	0	0	0	1	-1	2	-8.5
$\text{SOPu}(\text{OH})_3^0$	1	0	0	-4	0	0	0	1	-1	1	0.0

These reactions correspond to a matrix of stoichiometric coefficients given in Table 27.6. This table also gives the formation constants of plutonium hydroxyl and nitrate complexes in solution, Eqs. 27.53 through 27.57, which are taken from the thermodynamic database (Guillaumont et al. 2003). The equilibrium constants (Table 27.6) for surface complexes, Eqs. 27.41 through 27.52, were taken by analogy with thorium (Yeh et al. 1995).

In the calculations of molar concentrations of $[\text{SiOH}]^T$ (the boundary concentration for colloids) and $[\text{SOH}]^T$ (the initial concentration of adsorption sites on the rock) (Table 27.7) we assumed that the densities of adsorption sites of the mobile and immobile phases are the same, $N_S = 0.1 \text{ nm}^{-2}$ ($0.1 \cdot 10^{16} \text{ dm}^{-2}$), whence $N_{SA} = N_S/N_A = 1.66 \cdot 10^{-9} \text{ mol dm}^{-2}$. For the specific (weight) surface of colloids, $S_A = 100 \text{ m}^2 \text{ g}^{-1}$ ($10^7 \text{ dm}^2 \text{ kg}^{-1}$) (the characteristic value of clay mineral, illite), from formula (27.19) with colloid concentration in solution $C_S = 10 \text{ mg dm}^{-3}$ (basic variant), we obtain $[\text{SiOH}]^T = 1.66 \cdot 10^{-7} \text{ mol dm}^{-3}$. As the surface characteristic of the rock, we take the value $S_A = 0.001 \text{ m}^2 \text{ g}^{-1}$ ($10^2 \text{ dm}^2 \text{ kg}^{-1}$). With aquifer material density $\rho_b = 2.0 \text{ kg dm}^{-3}$ and the porosity $\phi = 0.2$, we have $[\text{SOH}]^T = 1.66 \cdot 10^{-6} \text{ mol dm}^{-3}$. The capacities of potential layers of both phases were specified to be the same: $C_1 = 1.0 \cdot 10^{-2} \text{ F dm}^{-2}$, $C_2 = 0.1 \cdot 10^{-2} \text{ F dm}^{-2}$.

Table 27.7 Initial and boundary total concentrations of components (basic variant)

Concentrations, mol/dm ³	Pu ⁴⁺	Na ⁺	NO ₃ ⁻	pH	SiOH	SOH
Initial (t = 0, x > 0)	1 · 10 ⁻¹²	1.6 · 10 ⁻³	4.3 · 10 ⁻³	7.0	1 · 10 ⁻¹¹	1.66 · 10 ⁻⁶
Boundary (t > 0, x = 0)	1 · 10 ⁻¹⁰	1.6 · 10 ⁻¹	4.3 · 10 ⁻¹	7.0	1.66 · 10 ⁻⁷	1.66 · 10 ⁻⁶

For definiteness sake we assume that the boundary concentration of NaNO₃ in all calculation variants is 500 mg L⁻¹. The initial concentration of this electrolyte is two orders of magnitude less. Table 27.7 also gives the initial and boundary concentrations of Pu(IV).

27.3.2.2 Calculation Results

As before, we will primarily proceed from the analysis of plots of the spatial distribution of Pu(IV) = $f(x)$. At the same time, we will use modeling results to evaluate the effective values of the coefficient of sorption distribution K_d , by which we mean the ratio of the concentration of Pu(IV) adsorbed on rock to its total concentration in liquid phase in the zone completely occupied by the solution entering the model domain (Table 27.7). In the base variant $K_d = 0.88 \text{ cm}^3 \text{ g}^{-1}$.

Example 1 demonstrates (Fig. 27.10) the effect of colloid particle concentration on the displacement velocity of concentration fronts. It can be seen that an increase (relative to the basic variant, 10 mg/L) in colloid concentration to 100 mg/L leads to about a threefold increase in plutonium migration velocity (the estimated value of $K_d = 0.09 \text{ cm}^3 \text{ g}^{-1}$). The low concentrations of colloids (0.001 mg L⁻¹) abruptly reduce the mass transport velocity ($K_d = 36.4 \text{ cm}^3 \text{ g}^{-1}$), so that within the calculation time, the concentration front shifts only several centimeters downstream of the inlet boundary. The curves in the resulting plot, corresponding to the solution of the fundamental problem with the specified K_d , confirm the possibility to use simplified calculation schemes in the independent analysis of the physicochemical state of the system under static conditions.

Example 2 illustrates the anticipated trend in the effect of pH of the boundary solution on the concentration distributions. As can be readily seen in Fig. 27.11, the sorption of Pu(IV) increases with increasing pH, hence a decrease in its migration velocity in the rock. However, such tendency can be seen only in the range pH < 6: higher values do not effect the migration velocity. By all appearance, at high pH, the sorption of Pu(IV) on the rock is hampered by the formation of hydroxyl complexes in solution.

Overall, model experiments demonstrate a high sensitivity of the process to the physicochemical state of the system and the need of multiparameter support of appropriate calculations, which is sometimes impracticable. This conclusion is also valid for other actinides. Moreover, the classical thermodynamic approach used here for the analysis of plutonium colloidal transport, may give an inadequate description

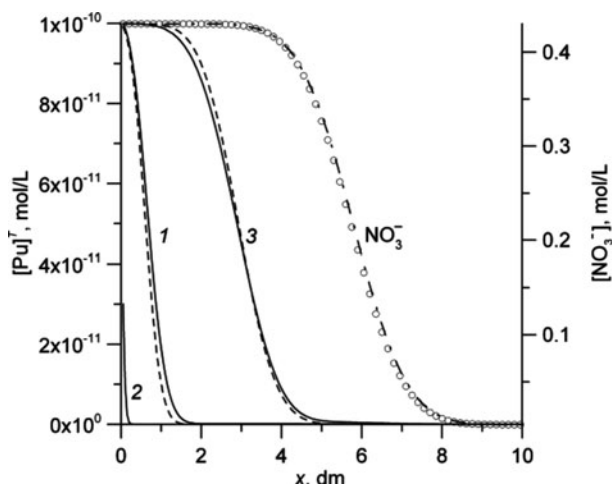


Fig. 27.10 The effect of colloid concentration on the character of concentration distributions (1) $C_{\text{coll}} = 10 \text{ mg/L}$ ($1.6610^{-7} \text{ mol/L}$), basic variant; (2) $C_{\text{coll}} = 0.001 \text{ mg/L}$ ($1.6610^{-11} \text{ mol/L}$); (3) $C_{\text{coll}} = 100 \text{ mg/L}$ ($1.6610^{-6} \text{ mol/L}$). The *dashed curves* are analytical estimates with $K_d = 0.88, 36.4, 0.09 \text{ cm}^3 \text{ g}^{-1}$, respectively. Here and in Fig. 27.11, the *dash-and-dot curve* is the distribution of NO_3^- ion; *hollow circles* show the analytical solution of the advection–dispersion equation for an inert (nonsorvable) component

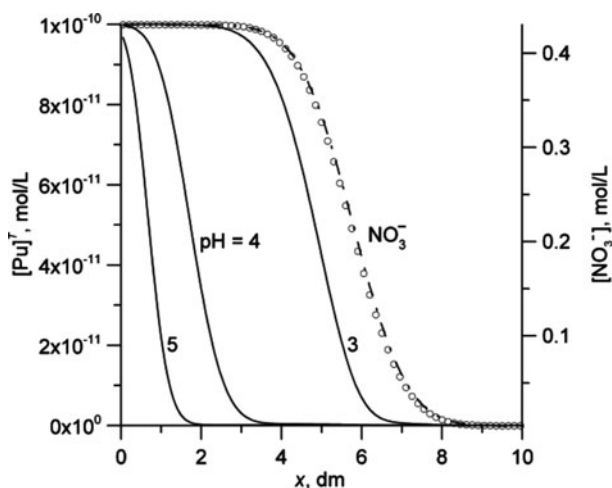


Fig. 27.11 The effect of solution pH on the character of concentration distributions (basic variant)

of this process because of the irreversibility in sorption of plutonium interacting with colloids. If sorption in the aquifer is irreversible, the obtained estimates are not conservative and the retention properties of aquifer material can be overestimated.

Apart from sorption-related reactions inside the liquid phase, a number of other physical and chemical processes are known to be important for plutonium in many cases. These include such factors as changes in the oxidation state of plutonium through redox transformations, the formation of chemical complexes with greater mobility, and the precipitation or co-precipitation of solid contaminant phases (Rai et al. 1980; Dai et al. 2002, 2005; Flury and Harsh 2003; Smith and Amonette 2006; Cantrell and Riley 2008). Therefore, despite the significant effort that has been expended on studying the migration of plutonium and other actinides, there remain significant areas of uncertainty.

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Conclusion

It is clear that the material considered in this monograph does not exhaust the wide diversity of hydrogeological problems whose solution requires the use of the apparatus of groundwater migration theory. The priority in the choice of the problems was primarily determined by the experience of the author in processing the actual (both field and laboratory) materials collected during studies at real hydrogeological sites. The author believes that this experience has clearly demonstrated that, methodologically, the integrated approach to studying phenomena of mass transfer accompanied by chemical reactions in the subsurface basing on the combination of analytical, numerical, and numerical–analytical methods of studies is most productive in both the solution of applied hydrogeological problems and conceptual model construction aimed at the development of basic knowledge about solute migration in the subsurface hydrosphere.

The author also hopes that this book will help the reader to see that to find effective solutions of some hydrogeological problems does not always require one to use extremely complex calculation algorithms involving the entire spectrum of possible migration mechanisms and hydrochemical interactions. Although the state-of-the-art in numerical modeling methods in hydrogeology allows the researcher to cope with problems of practically any complexity, the obtained results are commonly not convincing because it is difficult to properly evaluate all parameters of such numerical models. Therefore, the use of reasonably simplified analytical models, which were the main focus of this study, and, sometimes, expert estimates may yield more tangible and practically significant results. The solution of practical (engineering) problems is impossible without the involvement of diverse geological and experimental material and requires the results to be checked against alternative models. The hope to awake hydrogeologists' interest in the search for new, alternative solutions of the problems considered in this book was among the incentives for the author to write it.

Unfortunately, the prescribed, and thus limited, volume of this monograph failed to allow the author to consider some processes accompanying the *multiphase* flow of immiscible fluids denoted by the well-known abbreviation NAPLs and known most often to be hazardous groundwater pollutants often not less toxic than radionuclides. This range of multiphase flow problems also includes the description of motion in geological beds of liquefied greenhouse gases – a problem currently

very popular. Its solution is associated with the substantiation of one of the most efficient nature-conservative measures, namely, the sequestration of carbon dioxide in geological media in response to climate change, using, in particular, the capacity of deep saline aquifers to sequester this gas. The author's experience in such studies could serve as a basis for a special publication.

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