

**Mathematical models
of flow and contaminant transport
in saturated porous media**

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Well posed models that describe the transport of the mass of a fluid phases and of components of a fluid phase in saturated porous medium domains, regarded as *continua*, are presented and discussed.

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1. Introduction

The objective of these lectures is to discuss and present well posed models that describe the transport of the mass of fluid phases and of components of fluid phases in saturated porous medium domains regarded as *continua*. Domains containing sand, gravel and ceramics may serve as examples.

Let the symbol E_α denote the amount of an *extensive quantity*, E , in a phase denoted by the subscript α . The corresponding intensive quantity, or density of E , is denoted by e_α :

$$e_\alpha = \frac{E_\alpha}{\mathcal{U}_\alpha},$$

where \mathcal{U}_α indicates the volume of the α -phase. Examples of E are mass, momentum, and energy.

For the purpose of these lectures, a domain is defined as a *continuum* with respect to E_α , if e_α is defined at *every* point of the domain.

Let us start with a brief introduction of some commonly used definitions.

1.1. The porous medium continuum

A *porous medium* (plural: porous media) domain is a portion of space occupied partly by a *solid matrix* and partly by a *void space*; the latter is occupied by one or more fluid phases. Obviously, this definition is insufficient, as it says nothing about the actual distribution of these two portions within the domain. Intuitively, in view of the examples listed above, what is missing is something like "... and both the void space and the solid matrix are distributed over the considered domain". What we mean by this is that if we take sufficiently large samples of the porous material at different locations within a porous medium domain, we shall find *both* a solid phase and a void space in every one of them. However, if we wish to represent the behavior of the phases within a sample by averages taken over the volume

of such a sample, and assigning them to the center of the sample, the volume of the latter should be sufficiently small. We refer to the volume of a sample that satisfies these conditions, as a *Representative Elementary Volume* (abbreviated **REV**) (e.g., [3]) of the considered porous medium domain at the given point.

Why do we need to describe (= model) the behavior of the fluid and solid phases within a porous medium domain by averages? Let us use the term **microscopic level** to denote the level at which the behavior is described by referring to what happens at points *within* each phase. We shall use the term **macroscopic level** to denote the level at which the behavior of a phase at a point within a porous medium domain is described by averages of state variables and of geometrical properties of the phase configuration, taken over the REV centered at that point. Since the microscopic level of description is the real (?) one, we can ask, again, why not describe transport phenomena at that level, as we do, for example, in fluid or solid mechanics?

The answer is that although we can write the models that describe phenomena of transport—the mass balance equations, the flux equations, the constitutive relations, etc.—at the microscopic level, we *cannot* describe the geometry of the boundary that delineates each phase. Furthermore, we cannot measure the values of state variable, e.g., pressure at a point within a phase (that occupies the void space or part of it), in order to validate the model. By averaging over an REV, we obtain a description at the macroscopic level. Measurements, if taken over an REV, provide the information required for model *validation*. The advantage of modeling at the macroscopic level is obvious. However, the “payment” for this advantage (of circumventing the need to know the interphase boundaries) is the introduction of various (macroscopic) *coefficients* (e.g., porosity, permeability, dispersivity) that describe (at the macroscopic level) the effect of the microscopic interphase boundaries, the information about which we have avoided.

We have now explained why we have introduced the REV concept. By averaging the microscopic behavior over an REV, we obtain the description of that behavior at the macroscopic level. This description involves coefficients that can be determined only by experiments, combined with some procedure of “parameter estimation”, “model calibration”, or “solving the inverse problem”.

For a given porous medium domain, the size of the REV should be constrained in order to ensure the uniqueness of the averaged values of

state variables and of medium coefficients. The size of an REV must be sufficiently larger (say, 10-20 times) than the scale of heterogeneity at the microscopic level (resulting from the configuration of the phases within the REV), and much smaller (say, 100 times) than the characteristic length of the considered domain. When the domain is inhomogeneous at the macroscopic level, another upper limit should ensure that the variation of properties over the REV should be sufficiently close to linear, [3].

With the above discussion as background, we can now modify the definition of a porous medium given earlier. *A porous medium domain is a portion of space occupied partly by a solid matrix and partly by a void space, for which an REV can be identified.* Once a domain is identified as a porous medium, we can describe the transport of extensive quantities within it at the macroscopic level. At that level, every extensive quantity constitutes a continuum over the domain. The macroscopic level description is obtained by averaging the microscopic level over the REV.

Other “homogenization” techniques can also be used for passing from the microscopic level to the macroscopic one. In Subec. 4.4 we shall introduce another level of description—the *megascopic level*.

1.2. Model definition

A *model* may be defined as a *selected simplified version of a real system, and phenomena that take place within it, that approximately simulates the system's excitation-response relationships that are of interest.* For example, a ground water system may be ‘excited’ by pumping, by artificial recharge, or by changing a boundary condition. Its ‘response’ takes the form of spatial and temporal changes in water levels and in contaminant concentrations. Another example is when an aquifer is contaminated. The ‘excitation’ is the source of the contaminant, and the response takes the form of the spatial and temporal changes in concentration within the aquifer. Pumping from an aquifer and the resulting land subsidence, may serve as another example. With the above definition, all that a model can do is to *predict* the future behavior of an investigated system. Nevertheless, modeling activities may be conducted to achieve any of the following objectives:

- To predict the behavior of a considered system in response to excitations that stem from the implementation of management decisions.

- To obtain a better understanding of a considered system from the geological, hydrological, and chemical points of view.
- To provide information required in order to comply with regulations.
- To provide information for the design of a monitoring network, by predicting the system's future behavior.
- To provide information for the design of laboratory and field experiments.

Although a model is eventually expressed in mathematical terms, the mathematical notation is used merely as a compact way of describing the physical and chemical phenomena that are relevant to the considered problem. However, the mathematical formulation is needed if we wish predict the system's future behavior.

The first step in any modeling process is the establishment of the conceptual model of the considered problem and problem domain.

1.3. Conceptual model

The *conceptual model* of a problem and a problem domain consists of a set of assumptions, expressed *in words*, that reduce the real problem and the real domain to simplified versions that are satisfactory in view of the modeling objectives and the information that the model is expected to provide. Determining the conceptual model is the first, perhaps the most important, step in the modeling process. Once a conceptual model has been established, it is translated into a mathematical one.

Following is a list of typical aspects that require assumptions:

- The domain's hydrogeology, stratigraphy, etc.
- The geometry of the surface that bounds the domain of interest.
- The dimensionality of the model (one, two, or three dimensions).
- The behavior of the system: steady state or transient.
- The kind of soil and rock materials comprising the domain, as well as inhomogeneity, anisotropy, and deformability of these materials.
- The number and kinds of fluid phases and the relevant chemical species involved.
- The extensive quantities transported within the domain.
- The relevant material properties of the solid matrix (e.g. deformability)

and of fluid phases (density, viscosity, compressibility, Newtonian or non-Newtonian behavior).

- The relevant transport mechanisms within the domain.
- The possibility of phase change and exchange of chemical species between adjacent phases.
- The relevant chemical, physical, and biological processes that take place in the domain.
- The fluid flow regime involved (e.g., laminar or non-laminar).
- The existence of isothermal or non-isothermal conditions (and their effect on fluid phase properties and on chemical–biological processes).
- The presence of assumed sharp macroscopic fluid–fluid boundaries, such as a phreatic surface.
- The relevant state variables, and the areas or volumes over which averages of such variables are taken.
- The presence of sources and sinks of fluids and chemical species within the domain, and their nature.
- Initial conditions within the domain, and conditions on the domain's boundaries.

More items may be included in the conceptual model for specific cases.

It is recommended that these assumptions be numbered, say [A1], [A2], etc., as is done for equations, so that they can be referred to.

Unless otherwise specified, we shall assume that the flow regime is *laminar*, and that the considered fluid phase—water—is *Newtonian*. We shall also assume that the considered porous medium domain is such that the behavior of the phases in it can be described at the macroscopic, or continuum level. This is the level at which all variables are averages of their respective *microscopic* values over a Representative Elementary Volume (REV).

The macroscopic (continuum) description of flow, or of any other transport phenomenon, is derived by averaging the microscopic description over an REV of volume U_o . The macroscopic model obtained in this way describes the flow in terms of *macroscopic*, or averaged quantities.

The symbols E_α for an *extensive quantity* of an α -phase, e_α for the corresponding *intensive quantity*, or density, and U_α , for the volume of α , have already been introduced at the beginning of this chapter.

Two kinds of averages of e_α can be defined (Fig. 1):

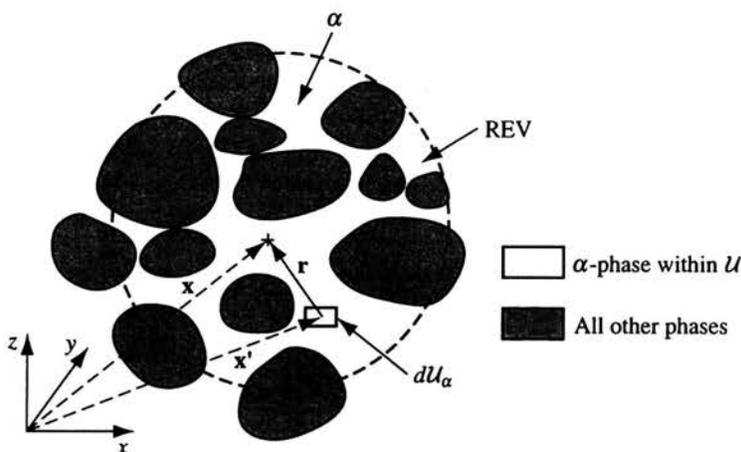


Figure 1: Nomenclature for averaging over an REV.

Intrinsic phase average. The intrinsic phase average of e_α , taken over the domain of the REV of volume U_o , centered at the point \mathbf{x} , is defined as:

$$\bar{e}_\alpha^\alpha(\mathbf{x}, t) = \frac{1}{U_{o\alpha}(\mathbf{x}, t)} \int_{U_{o\alpha}(\mathbf{x}, t)} e_\alpha(\mathbf{x}', t; \mathbf{x}) dU_\alpha(\mathbf{x}'), \quad (1.1)$$

where $U_{o\alpha}$ is the volume of the α -phase within U_o , and \mathbf{x}' is a point in the REV centered at \mathbf{x} . The *intrinsic phase average* is, thus, an average of E_α per unit volume of the considered phase.

Phase average. The phase average of e_α is defined as:

$$\bar{e}_\alpha(\mathbf{x}, t) = \frac{1}{U_o} \int_{U_{o\alpha}(\mathbf{x}, t)} e_\alpha(\mathbf{x}', t; \mathbf{x}) dU_\alpha(\mathbf{x}'). \quad (1.2)$$

This is an average of E_α per unit volume of porous medium. The two kinds of averages are related to each other by:

$$\bar{e}_\alpha = \theta_\alpha \bar{e}_\alpha^\alpha, \quad (1.3)$$

where

$$\theta_\alpha = \frac{U_{o\alpha}}{U_o} \quad (1.4)$$

is the *volumetric fraction* of the α -phase within U_o .

The discussion in these lectures is at the macroscopic level. Hence, unless otherwise specified, no special symbol is used to indicate this fact.

1.4. Mathematical model

The conceptual model is “translated” into a mathematical model, the solution of which, subject to specified initial and boundary conditions, provides the information required for making management decisions.

Each mathematical model consists of the following items:

- The *geometry* of the surface that bounds the considered domain.
- *Partial differential equations* that express the *balances* of the considered extensive quantities (e.g., mass of fluids, mass of chemical species, energy)¹.
- *Flux equations* that relate the fluxes of the considered extensive quantities to the relevant state variables of the problem.
- *Constitutive equations* that define the behavior of the particular phases and chemical species involved (e.g., dependence of density and viscosity on pressure, temperature, and solute concentration).
- *Sources and sinks* of the relevant extensive quantities.
- *Initial conditions* that describe the *known* state of the considered system at some initial time.
- *Boundary conditions* that describe the interaction of the considered domain with its environment (i.e., outside the delineated domain) across their common boundaries.

1.5. General macroscopic balance equation

The core of any mathematical model that describes the transport of an *extensive quantity* is a partial differential equation (p.d.e.) that expresses the balance of that quantity. At the microscopic level, we obtain this equation by writing the balance of an extensive quantity for a small volume of a phase centered at a point, and then letting this volume be gradually reduced to zero. We refer to this approach as the *Lagrangian approach*.

The general *microscopic balance equation* for any extensive quantity of a fluid phase, E , having a density e , can be expressed in the (vector) form:

$$\frac{\partial e}{\partial t} = -\nabla \cdot (e\mathbf{V} + \mathbf{j}^E) + \rho\Gamma^E, \quad (1.5)$$

¹Momentum, as an extensive quantity, is not mentioned, as in the models considered here, the momentum balance is introduced in its simplified form of Darcy's law.

where \mathbf{V} is the mass-weighted velocity of the fluid phase, \mathbf{j}^E is the *diffusive flux* of E , relative to \mathbf{V} , ρ denotes the phase mass density, and Γ^E denotes the source of E , expressed as E per unit mass of the phase per unit time. Each term in this equation expresses added E per unit volume of the fluid phase.²⁾

The diffusive flux of E is related to the velocity, \mathbf{V}^E , of the E -continuum, by:

$$\mathbf{j}^E = e (\mathbf{V}^E - \mathbf{V}).$$

By averaging (1.5) over the considered α -phase within an REV, we obtain the general macroscopic balance equation for E in the form, [3]:

$$\begin{aligned} \frac{\partial \theta \bar{e}^\alpha}{\partial t} = & - \nabla \cdot \theta (\bar{e}^\alpha \bar{\mathbf{V}}^\alpha + \bar{\tilde{e}} \bar{\mathbf{V}}^\alpha + \bar{\mathbf{j}}^E) \\ & - \frac{1}{\mathcal{U}_o} \int_{\mathcal{S}_{\alpha\beta}} [e(\mathbf{V} - \mathbf{u}) + \mathbf{j}^E] \cdot \mathbf{n} dS + \theta \bar{\rho} \Gamma^E, \end{aligned} \quad (1.6)$$

where θ and $\bar{\mathbf{V}}^\alpha$ denote the volumetric fraction and the (mass averaged) velocity, respectively, of the considered phase, \mathbf{n} denotes the outward unit vector normal to the (microscopic) surface $\mathcal{S}_{\alpha\beta}$, between the α -phase and all other (β -)phases within the REV, and we have made use of the decomposition of the (intrinsic phase) averaged advective flux of E within the α -phase, $\bar{e} \bar{\mathbf{V}}^\alpha$, into two fluxes (to be discussed later): a macroscopic advective flux $\bar{e}^\alpha \bar{\mathbf{V}}^\alpha$, and another macroscopic flux, $\bar{\tilde{e}} \bar{\mathbf{V}}^\alpha$. In this equation:

- The flux $\bar{\tilde{e}} \bar{\mathbf{V}}^\alpha$, which is the flux of E in excess of the average advection of E carried by the phase, is the *dispersive flux* of E .
- The term

$$\frac{1}{\mathcal{U}_o} \int_{\mathcal{S}_{\alpha\beta}} [e(\mathbf{V} - \mathbf{u}) + \mathbf{j}^E] \cdot \mathbf{n} dS \equiv f_{\alpha \rightarrow \beta}^E$$

expresses the flux of E from the α to all β -phases, across the $\mathcal{S}_{\alpha\beta}$ -surface, which separates the α -phase from all other β -phases within \mathcal{U}_o , by advection relative to the possibly moving $\mathcal{S}_{\alpha\beta}$ -surface that moves at a velocity \mathbf{u} , and by diffusion, \mathbf{j}^E .

More about the diffusive and dispersive fluxes is presented in Chap. 1.3.

²⁾Always remember that "for any extensive quantity, *minus the divergence of a flux* expresses the excess of inflow over outflow, per unit volume and per unit time."

1.6. Boundary surface

A considered porous medium domain is separated from its environment by a boundary surface. The environment may be devoid of porous medium, or it may consist of a different porous medium.

Figure 2, [3], shows four regions: a region with no void space, two regions containing solid matrices of different porosity, and a region with no solid matrix. By employing the methodology of averaging over an REV in order to

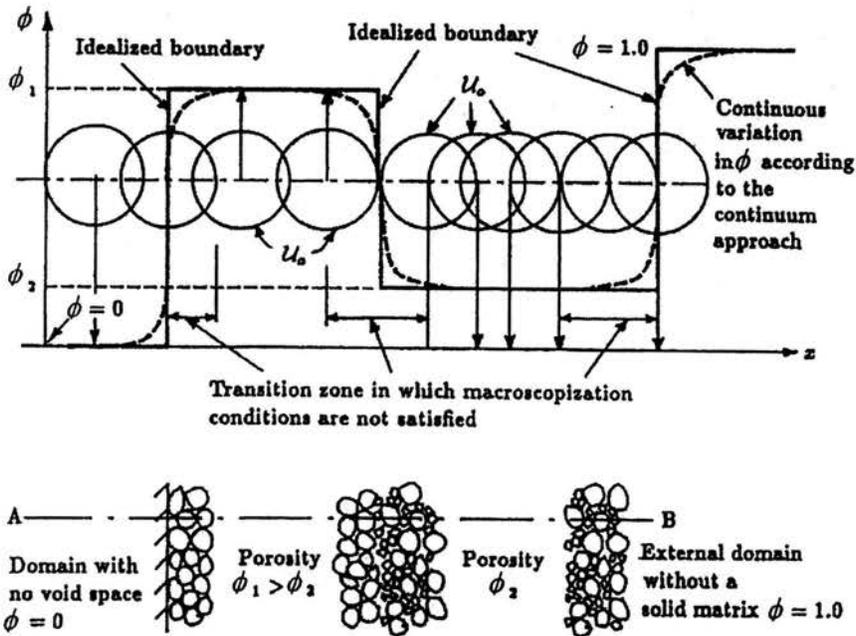


Figure 2: Introduction of abrupt macroscopic boundaries, [3]

determine the porosity variations, we note that the latter varies *gradually* as we move along AB. Although we observe rather steep changes in porosity, no abrupt change occurs. Thus, in the continuum sense, sharp boundaries that delineate the different media *at the macroscopic level*, do not exist. Instead, we replace the actual variation in porosity in every region of transition, by an *idealized boundary in the form of a surface across which an abrupt change in porosity takes place*. The boundary surfaces introduced in this way, divide the entire domain and its vicinity into sub-domains separated from each other by

sharp boundary surfaces. The continuum approach is applicable to each sub-domain. Across the boundaries, we *assume* the existence of a jump in porosity and in other macroscopic matrix properties. On the two sides of each such boundary, the values of these properties are obtained by extrapolating the spatial linear trend in property values, as the boundary is approached from within each sub-domain. The sharp boundary may be arbitrarily located at any point within the transition region. For convenience, however, we usually locate it at the point corresponding to the mean porosity between the two adjacent regions (Fig. 2). In this way we *hypothesize* the existence of regular continuum domains for all phases present in the system *up to the boundary surface* on both its sides. The jump in porosity leads also to a jump in *areal porosity*. This entails the presence of fluid - fluid, fluid - solid, solid-fluid and solid-solid segments along the boundary. Obviously, in reality no such jumps occur. However, recalling the definition of a model, our *conceptual model assumes* an abrupt change in the continuum properties across the boundary surface.

The considered porous medium domain is delineated by boundary surfaces. Let $F(\mathbf{x}, t) = 0$ represent the equation of a possibly moving (macroscopic) boundary surface. The speed of displacement of this boundary, \mathbf{u} , should not be mixed up with the velocities of the fluids present on both sides of the surface. As the surface moves, its shape may change, but its equation, $F(\mathbf{x}, t) = 0$, remains unchanged. The quantity F is, thus, a conservative property of the points on the surface, for which the total derivative vanishes, i.e.,

$$\frac{D F}{D t} \equiv \frac{\partial F}{\partial t} + \mathbf{u} \cdot \nabla F = 0. \quad (1.7)$$

By definition, the unit vector, \mathbf{n} , normal to the surface $F = 0$, is given by:

$$\mathbf{n} = \frac{\nabla F}{|\nabla F|}. \quad (1.8)$$

From (1.7), we obtain:

$$\mathbf{u} \cdot \nabla F = -\frac{\partial F}{\partial t}. \quad (1.9)$$

The component of \mathbf{u} normal to the surface is then given by:

$$u_n \equiv \mathbf{u} \cdot \mathbf{n} = -\frac{\partial F / \partial t}{|\nabla F|} = -\frac{\partial F / \partial t}{\partial F / \partial s_n}, \quad (1.10)$$

where s_n is a distance measured along \mathbf{n} .

1.7. Phases and components

A *chemical species* is defined as an identifiable homogeneous chemical compound (element, ion, or molecule) that participates as an entity (whether as a reactant or as a product) in a chemical reaction that takes place within a phase. The term 'chemical species' thus refers to the actual form in which a molecule or ion is present in a phase, or in a solution. For example, the element *iodine* in an aqueous solution may exist in the form of one or more species, e.g., I_2 , I^- , HIO , IO^- , IO_3^- . The same compound in solution and as an adsorbate on a solid are considered as *two* different species. Similarly, the same compound present in different phases are considered different species.

A *phase* may be defined as a portion of space occupied by a material such that its behavior is described by a single set of constitutive relations, for example, the relationship between density, pressure, and temperature. This definition also enables us to refer to disjoint portions of space occupied by the same material, e.g., an assembly of *ganglia* of a distinct liquid embedded in another liquid, immiscible with the first, as a *single* liquid phase.

Another, not rigorous, but more descriptive way is to define a phase as the homogeneous portion of space, whether interconnected or not, that is separated from other such portions by a well defined sharp physical (and observable) *interphase boundary*, or *interface*. There can be only one gaseous phase in the void space of a porous medium domain, because all gaseous phases are completely *miscible*, and cannot maintain a distinct interface between them. Two *miscible liquids* also constitute a single phase.

Often, a chemical species, initially present in one fluid phase, will cross an interfacial boundary and diffuse into an adjacent fluid phase. Nevertheless, as long as a sharp interface is maintained between the two fluids, we regard them as separate, albeit miscible, phases.

A phase may be composed of a large number of chemical species. However, under conditions of *chemical equilibrium*, the number of independent chemical species necessary to completely describe the composition of a given phase may be much smaller. We shall use the term *component* to denote a chemical species that belongs to the smallest set of such species that is required to completely define the chemical composition of a phase under equilibrium conditions. In the absence of chemical equilibrium, all species are defined as components.

Often, only a subset of the species within a phase is in equilibrium. Then, the set of components consists of the components of the system that are in equilibrium, together with the species that are not in equilibrium.

For the sake of simplicity, we shall often use the term ‘component’ also to denote a mixture of a number of independent chemical species in a liquid or a gas. The selection of components is not unique, in the sense that different chemical species, or assembly of species, may be selected as components of a given phase.

1.8. Homogeneity and isotropy

We consider the macroscopic geometrical properties characterizing the configuration of the void space or of any phase within the REV of a porous medium (e.g., porosity, volumetric fraction of a phase, permeability). A porous medium *domain* is said to be *homogeneous* with respect to a macroscopic geometrical property if that property has the same value *at all points of the domain*. If not, the domain is called *heterogeneous*, or *nonhomogeneous*, with respect to that property. For example, a porous medium domain is homogeneous with respect to porosity, ϕ , if $\nabla\phi = 0$ everywhere within that domain.

A porous medium is said to be *anisotropic at a (macroscopic) point with respect to a property* if that property varies with direction at that point. For example, the resistance of a porous material to the transport of various extensive quantities, such as mass or heat, through it, may vary with direction. A porous medium is said to be *isotropic at a point with respect to a given property*, if that property does not vary with direction at that point. A typical porous medium property that exhibits anisotropy is permeability.

2. Modeling flow in a three-dimensional domain

The model will be written at the macroscopic level. All variables are averages of their respective values at the microscopic level. Nevertheless, we shall not use any symbol to indicate this fact.

2.1. Conceptual model

Although as we develop the model, we may add more assumptions, the basic underlying conceptual model consists of the following assumptions:

- The flow domain is delineated by boundary surfaces. Each boundary surface segment is described by an equation of the form $F = F(x, y, z, t)$.
- The state variable is water pressure, $p = p(\mathbf{x}, t)$, or *piezometric head*:

$$h = h(\mathbf{x}, t) = z + \frac{p}{\rho g}, \quad (2.1)$$

where the position vector \mathbf{x} denotes a point in the three-dimensional domain. For a variable density, we cannot use the piezometric head as a variable. When the water is assumed to be compressible, i.e., $\rho = \rho(p)$, the piezometric head is replaced by *Hubbert's potential*, defined as:

$$h^* = z + \int_{p_o}^p \frac{dp}{g\rho(p)}, \quad (2.2)$$

in which p_o is a reference pressure, and g is the gravity acceleration. The case of variable density, due to variations in solute concentration, is discussed in Sec. 5.

- The solid matrix is deformable. However, unless we are interested in analyzing stresses and strains in the domain, we introduce certain approximations that enable us to include the effect of solid matrix deformability on water storativity (see below), without solving in detail for the strain distribution in the considered domain.

- The two major porous medium properties are:

* **Hydraulic conductivity**, $\mathbf{K} = \mathbf{K}(x, y, z)$ (dims. L/T). In an *anisotropic* porous medium, \mathbf{K} is a second rank symmetric tensor.

* **Specific storativity** $S_o = S_o(x, y, z)$ (dims. L⁻¹), due to the compressibility of the water and the solid matrix). The specific storativity is defined as the *volume of water added to (or released from) storage in a unit volume of porous medium per unit increase (or decline) in piezometric head*. The release is assumed to be instantaneous upon decline of head.

- The flow is laminar, so that its *specific discharge* (= discharge per unit area of porous medium), \mathbf{q}_r (dims. L/T), relative to the possibly moving solid matrix, is expressed by *Darcy's law* (in vector form):

$$\mathbf{q}_r \equiv \phi(\mathbf{V} - \mathbf{V}_s) = -\mathbf{K} \cdot \nabla h, \quad (2.3)$$

where \mathbf{V} and \mathbf{V}_s denote the (averaged) fluid and solid matrix velocities (dims. L/T), respectively, ϕ is the porosity, and \mathbf{K} (dims. L/T) denotes the hydraulic conductivity tensor. For a compressible fluid, we replace h by *Hubbert's potential*, h^* , defined by (2.2).

For the general case of $\rho = \rho(p, c, T)$, where c represents the concentration of dissolved matter, Darcy's law takes the form:

$$\mathbf{q}_r = -\frac{\mathbf{k}}{\mu} (\nabla p + \rho g \nabla z), \quad (2.4)$$

where \mathbf{k} denotes the *permeability tensor*. For a stationary non-deformable porous medium, $\mathbf{q}_r \equiv \mathbf{q} = \phi \mathbf{V}$. For a constant ρ and μ , $\mathbf{K} = \mathbf{k} \rho g / \mu$.

- Pumping and artificial recharge (= injection) may take place through wells that take the form of point sources or sinks. For a point sink, at the point \mathbf{x}^m , the rate of pumping is denoted as $P^m(\mathbf{x}, t)$ ($P^m < 0$ for pumping and $P^m > 0$ for injection). In reality, a well has the form of a vertical line segment at a (more or less) constant head. Then, the distribution of discharge rate along it is uneven (and *a-priori* unknown). Such an elongated screen may be represented as an array of closely spaced point sources or sinks.

2.2. Mass balance equation

The extensive quantity under consideration is the mass of a fluid phase, $E = m$. The corresponding intensive quantity is $e = \rho$, i.e., the mass density

of the fluid continuum (= mass per unit volume of fluid phase). The velocity of the mass continuum is the weighted mass averaged velocity of the fluid, $\mathbf{V}^E = \mathbf{V}^m \equiv \mathbf{V}$. Although our objective is to discuss models of saturated flow and transport, occasionally, we shall extend the discussion to a fluid phase that occupies only part of the void space, in a multi-phase situation. For saturated flow, we replace the volumetric fraction of the α -phase, θ_α , by the porosity, ϕ .

The averaged, or macroscopic mass balance equation for an α -fluid phase that occupies a volumetric fraction θ_α (= ϕS_α), where S_α denotes the saturation of the α -phase, can be obtained by applying (1.6) to the case $e = \rho_\alpha$. Assuming that the dispersive flux of the mass (to be discussed in Subs. 4.1.4) is much smaller than its advective one, i.e., $|\overline{\rho \mathbf{V}^\alpha}| \ll |\overline{\rho^\alpha \mathbf{V}^\alpha}|$ (can be added to the conceptual model), we obtain the mass balance in the form:

$$\frac{\partial}{\partial t}(\theta_\alpha \rho_\alpha) = -\nabla \cdot (\rho_\alpha \mathbf{q}_\alpha) + \rho_\alpha \Gamma_\alpha, \tag{2.5}$$

where $\mathbf{q}_\alpha = \theta_\alpha \mathbf{V}_\alpha$ denotes the *specific discharge* (= flux) of the α -phase. For saturated flow, $S_\alpha = 1$, and we replace θ_α by ϕ . The symbol Γ_α denotes a source of the α -fluid (= added volume of α -phase per unit volume of porous medium, per unit time), other than through the (microscopic) $\mathcal{S}_{\alpha\beta}$ -interface. We regard a sink as a negative source. To obtain (2.5), we have assumed that the microscopic boundaries of the α -phase are material surfaces, so that $(\mathbf{V} - \mathbf{u}) \cdot \mathbf{n} = 0$ in (1.6). The above equation can be written for each of the fluids that together occupy the void space, e.g., $\alpha = w, a$, for water and air, respectively.

Let us consider the case of two fluid phases (air and water), in the absence of evaporation or air dissolution. The macroscopic mass balance equation for the water can be obtained from: (2.5) in the form:

$$\frac{\partial}{\partial t}(\phi S_w \rho_w) = -\nabla \cdot (\rho_w \mathbf{q}_w) + \rho_w \Gamma_w. \tag{2.6}$$

The symbol Γ_w denotes a source of water (= added volume per unit volume of porous medium, per unit time), other than through the (microscopic) \mathcal{S}_{wa} -interface. Although, as explained above for the microscopic equation, in the rigorous sense, there cannot be a distributed source of mass in a three-dimensional space, we have, symbolically, introduced such a source here. It denotes an *external* source of water mass that takes the form of individual points at which water is injected. A negative value means withdrawal of

water from the void space, e.g., water imbibed by distributed roots may be approximated as a distributed water sink in a 3-d domain.

By changing α to a in (2.5), we obtain the mass balance equation for air under the same conditions.

For constant ρ_w and ρ_a , the mass balance equations for water and for air, reduce to

$$\frac{\partial(\phi S_w)}{\partial t} = -\nabla \cdot \mathbf{q}_w + \Gamma_w, \quad \frac{\partial(\phi S_a)}{\partial t} = -\nabla \cdot \mathbf{q}_a + \Gamma_a. \quad (2.7)$$

For saturated flow, i.e., when water fills the entire void space, $S_w = 1$ in the macroscopic water balance equation, and (2.6) reduces to

$$\frac{\partial(\phi \rho_w)}{\partial t} = -\nabla \cdot (\rho_w \mathbf{q}_w) + \rho_w \Gamma_w, \quad (2.8)$$

where $\mathbf{q}_w = \phi \mathbf{V}_w$ is the *specific discharge* of water. This equation may also be written in indicial notation, in the form:

$$\frac{\partial(\phi \rho_w)}{\partial t} = \frac{\partial(\rho_w q_{wi})}{\partial x_i} + \rho_w \Gamma_w. \quad (2.9)$$

By inserting appropriate expression for the fluxes appearing in the balance equations, we obtain *flow equations*. These describe the flow in terms of the state variable(s) of the system—usually pressure, piezometric head, or saturation.

2.2.1. Deformable porous medium

In a deformable porous medium, we have time-varying porosity and a moving solid matrix, i.e., $\partial\phi/\partial t \neq 0$, and $\mathbf{V}_s \neq 0$, where \mathbf{V}_s ($\equiv \overline{\mathbf{V}_s^s}$) is the macroscopic velocity of the solid matrix. Since Darcy's law expresses the fluid's flux relative to the solid, when considering flow through a deformable porous medium, we have to write the water and air mass balance equations in terms of the relative fluxes:

$$\mathbf{q}_{rw} = \phi S_w (\mathbf{V}_w - \mathbf{V}_s) \quad \text{and} \quad \mathbf{q}_{ra} = \phi S_a (\mathbf{V}_a - \mathbf{V}_s).$$

Because these expressions involve the solid's velocity, we have to consider also the mass balance equation for the solid. Henceforth, we shall limit the discussion to saturated flow only.

We can make use of the general balance equation (1.6), with $e = \rho_s$, $\theta = 1 - \phi$, $\mathbf{V} = \mathbf{V}_s$, $\mathbf{j}^E = 0$, $\Gamma^E = 0$, and assume that at the microscopic level, $(\mathbf{V}_s - \mathbf{u}) \cdot \mathbf{n} = 0$, i.e., the solid-fluid interface is a *material surface* with respect to the solid's mass. Then, the mass balance equation for the solid takes the form:

$$\frac{\partial}{\partial t}(1 - \phi)\rho_s = -\nabla \cdot [(1 - \phi)\rho_s \mathbf{V}_s]. \tag{2.10}$$

Introducing the *material* (or *total* or *substantial*) *time derivative* for the solid phase, defined by

$$\frac{D_s(\dots)}{Dt} = \frac{\partial(\dots)}{\partial t} + \mathbf{V}_s \cdot \nabla(\dots),$$

equation (2.10) can be rewritten in the form

$$\frac{1}{1 - \phi} \frac{D_s(1 - \phi)}{Dt} + \frac{1}{\rho_s} \frac{D_s \rho_s}{Dt} = -\nabla \cdot \mathbf{V}_s. \tag{2.11}$$

The deformation of the solid phase (not the solid matrix!) is usually assumed to be volume preserving. This means that at the *microscopic* level, $\nabla \cdot \mathbf{V}_s = 0$, and $D_s \rho_s / Dt = 0$. Hence, at the macroscopic level, $D_s \rho_s / Dt$ vanishes, so that (2.11) reduces to

$$\frac{1}{1 - \phi} \frac{D_s(1 - \phi)}{Dt} = -\nabla \cdot \mathbf{V}_s. \tag{2.12}$$

The left hand side of (2.12) may be interpreted as ‘the relative rate of expansion of the volume occupied by the solid phase.’

A detailed analysis of soil deformability requires the introduction of the soil's (macroscopic) *volumetric strain*, or *dilatation*, ε_{sk} . Denoting the (macroscopic) displacement of the soil's solid skeleton by \mathbf{w} , the soil's volumetric strain is expressed by:

$$\varepsilon_{sk} = \nabla \cdot \mathbf{w}. \tag{2.13}$$

Then, because

$$\mathbf{V}_s \equiv \frac{D_s \mathbf{w}_s}{Dt} \approx \frac{\partial \mathbf{w}}{\partial t}, \tag{2.14}$$

equation (2.12) becomes:

$$\frac{\partial \varepsilon_{sk}}{\partial t} = -\frac{1}{1 - \phi} \frac{D_s(1 - \phi)}{Dt}. \tag{2.15}$$

We now rewrite (2.8) in the following form:

$$\begin{aligned}
 \frac{\partial \phi \rho_w}{\partial t} &= -\nabla \cdot \phi \rho_w (\mathbf{V}_w - \mathbf{V}_s) - \nabla \cdot (\phi \rho_w \mathbf{V}_s) + \rho_w \Gamma_w \\
 &= -\nabla \cdot (\rho_w \mathbf{q}_{rw}) - \mathbf{V}_s \cdot \nabla (\phi \rho_w) - \phi \rho_w \nabla \cdot \mathbf{V}_s + \rho_w \Gamma_w \\
 &= -\nabla \cdot (\rho_w \mathbf{q}_{rw}) - \mathbf{V}_s \cdot \nabla (\phi \rho_w) \\
 &\quad + \phi \rho_w \frac{1}{1 - \phi} \frac{D_s(1 - \phi)}{Dt} + \rho_w \Gamma_w,
 \end{aligned} \tag{2.16}$$

or

$$\phi \frac{D_s \rho_w}{Dt} + \rho_w \frac{1}{1 - \phi} \frac{D_s \phi}{Dt} = -\nabla \cdot (\rho_w \mathbf{q}_{rw}) + \rho_w \Gamma_w. \tag{2.17}$$

For a *stationary non-deformable solid matrix*, $D_s(1 - \phi)/Dt = 0$, and $\mathbf{V}_s = 0$. Under these conditions, (2.16) reduces to (2.8).

Assuming that in a deformable porous medium,

$$\text{(a) } \left| \frac{\partial \rho_w}{\partial t} \right| \gg |\mathbf{V}_s \cdot \nabla \rho_w|, \quad \text{(b) } \left| \frac{\partial \phi}{\partial t} \right| \gg |\mathbf{V}_s \cdot \nabla \phi|, \tag{2.18}$$

i.e., assuming that spatial variations are much smaller than temporal ones, (2.17) reduces to

$$\phi \frac{\partial \rho_w}{\partial t} + \rho_w \frac{1}{1 - \phi} \frac{\partial \phi}{\partial t} = -\nabla \cdot (\rho_w \mathbf{q}_{rw}) + \rho_w \Gamma_w. \tag{2.19}$$

Finally, if we assume that:

$$\left| \phi \frac{\partial \rho_w}{\partial t} \right| \gg |\mathbf{q}_{rw} \cdot \nabla \rho_w|, \tag{2.20}$$

which may be interpreted as stating that the temporal rate of density change at a point is much larger than the spatial one, we may approximate $\nabla \cdot (\rho_w \mathbf{q}_{rw})$ in (2.19) by $\rho_w \nabla \cdot \mathbf{q}_{rw}$. For example, the mass balance equation (2.19) then reduces to

$$\phi \frac{\partial \rho_w}{\partial t} + \rho_w \frac{1}{1 - \phi} \frac{\partial \phi}{\partial t} = -\rho_w \nabla \cdot \mathbf{q}_{rw} + \rho_w \Gamma_w. \tag{2.21}$$

The second term on the l.h.s. of the above equations expresses the temporal rate of change in porosity, or the volume strain of the solid skeleton. These have to be expressed in terms of the variable(s) of the problem, e.g.,

in terms of the rate of change in water pressure. To achieve this goal, we introduce the concept of *effective stress* in the next subsection. Then, in Subs. 2.2.3, we shall discuss the fluid's specific storativity, and, at the end of that subsection, derive a different form for the mass balance equations for a deformable porous medium.

2.2.2. Effective stress and complete flow model

By writing the averaged momentum balance equations for the fluids that occupy the entire void space and for the solid within an REV, neglecting the inertial terms and those that express friction *within* the fluid, and summing up the two equations (in order to eliminate terms representing momentum exchange across fluid-solid interfaces), we obtain, [3] the *equilibrium equation*:

$$\nabla \cdot \bar{\sigma} + \bar{\rho} \mathbf{F} = 0, \tag{2.22}$$

in which, using the definition of phase average (Subsec. 1.3), $\bar{\sigma}$ is the *total stress* at a point in a (three-dimensional domain) given by

$$\bar{\sigma} = \frac{1}{\mathcal{U}_o} \int_{\mathcal{U}_o} \sigma \, d\mathcal{U} = \frac{1}{\mathcal{U}_o} \sum_{\alpha=f,s} \int_{\mathcal{U}_{o\alpha}} \sigma_{\alpha} \, d\mathcal{U}_{\alpha} = \bar{\sigma}_f + \bar{\sigma}_s, \tag{2.23}$$

where $\bar{\rho} \mathbf{F}$ ($= -\bar{\rho} g \nabla z$) denotes the gravity force acting on the total mass within the REV, and all stresses are second rank symmetric tensors.

In order to deal with a deformable porous medium, we use the concept of *effective stress* introduced in soil mechanics by Terzaghi, [14]. Essentially, this concept assumes that in a granular porous medium, the pressure in the water (or in the fluids in a multi-phase system) that *almost* completely surrounds each solid grain, produces on the latter a stress of equal magnitude, without contributing to the deformation of each grain. Instead, deformation occurs mainly due to the forces at the points of contact between the grains. At these points, concentrated normal and shear forces are transmitted from grain to grain. Thus, the (macroscopic) *strain-producing stress*, or *intergranular stress*, or *effective stress*, is obtained by subtracting the water pressure (or, in a multi-phase system, some average pressure of the fluids in the void space) from the stress in the solid material (all stresses and pressures being averaged ones).

The deformation of the solid matrix is produced mainly by the rearrangement of the grains, with localized slipping and rolling, and is largely

irreversible. A change in water pressure, with an equal change in total stress, produces no deformation and, hence, should produce no change in the effective stress. The deformation of the solid itself is neglected in considering porous medium deformation.

To illustrate the concept of effective stress in a simple way, let us limit the discussion for the moment to *vertical forces only*, and consider the vertical cross-section through a saturated porous medium domain and the horizontal unit area, AB, shown in Figure 3. In this section we shall make use of the

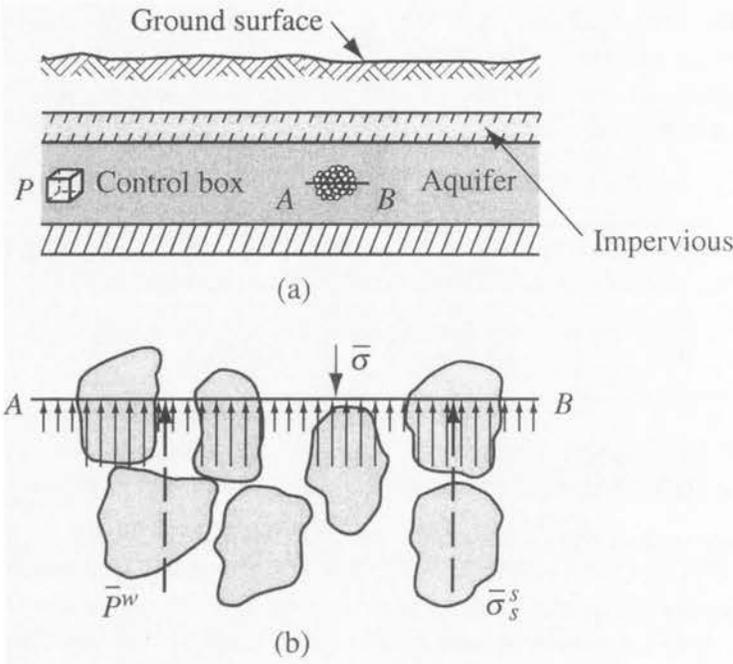


Figure 3: Nomenclature for the definition of effective stress.

special symbols used to indicate average, or macroscopic values, in order to emphasize the meaning of these averaged values.

At every instant, the load acting on the upper side of AB is due to the weight of soil, water, and any load that exists at ground surface. This load, which produces a (macroscopic) stress, $\bar{\sigma}$ (= total force per unit area of porous medium), must be in equilibrium with two stresses acting on AB from below: a stress, $\phi\bar{p}_w^w$, resulting from the (average) pressure in the water, \bar{p}_w^w , acting on the water portion of AB, and a stress $(1 - \phi)\bar{\sigma}_s^s$, resulting from the

(average) stress, $\overline{\sigma}_s^s$, in the solid skeleton, acting on the solid portion of AB. Both \overline{p}_w^w and $\overline{\sigma}_s^s$ are intrinsic phase averages, while $\overline{\sigma}$ is a volume average of σ . It can be shown (e.g., [3]) that these intrinsic phase averages are equal to intrinsic areal averages, that is, \overline{p}_w^w and $\overline{\sigma}_s^s$ also express force per unit area of water and per unit area of solid, respectively. The shear stress in the water has been neglected.

With the stresses $\overline{\sigma}$ and $\overline{\sigma}_s^s$ taken as positive for tension, but pressure in the water taken as positive for compression (as is common in fluid mechanics), the above statement of force (actually, stress) equilibrium can be expressed in the form:

$$\overline{\sigma} = (1 - \phi)\overline{\sigma}_s^s - \phi\overline{p}_w^w. \tag{2.24}$$

In order to express the above equation in terms of Terzaghi's effective stress, $\overline{\sigma}'_s$, defined as

$$\overline{\sigma}'_s = (1 - \phi)(\overline{\sigma}_s^s + \overline{p}_w^w), \tag{2.25}$$

we add and subtract $(1 - \phi)\overline{p}_w^w$ on the r.h.s. of (2.24), obtaining

$$\overline{\sigma} = (1 - \phi)\overline{\sigma}_s^s - (1 - \phi)\overline{p}_w^w - \phi\overline{p}_w^w + (1 - \phi)\overline{p}_w^w, \tag{2.26}$$

or:

$$\overline{\sigma} = \overline{\sigma}'_s - \overline{p}_w^w. \tag{2.27}$$

Although (2.24) through (2.25) are based on the *simplification of vertical stress only*, they can easily be extended to three-dimensional domains in the following manner. The (phase average) stress in the water may be decomposed into two parts, using the definition:

$$\overline{\sigma}_w^w = \overline{p}_w^w \mathbf{I} + \overline{\tau}_w^w,$$

where $\overline{\tau}_w^w$ is the (intrinsic phase average) shear (or deviatoric) stress in the water. Neglecting $\overline{\tau}_w^w$, and defining the effective stress as:

$$\overline{\sigma}'_s = (1 - \phi)(\overline{\sigma}_s^s + \overline{p}_w^w \mathbf{I}), \tag{2.28}$$

the total stress in a three-dimensional saturated medium is expressed by

$$\overline{\sigma} = \overline{\sigma}'_s - \overline{p}_w^w \mathbf{I}. \tag{2.29}$$

When changes take place, either in the external load (producing changes in the total stress distribution, $\bar{\sigma}$), or in the water pressure, \bar{p}_w^w , we have:

$$d\bar{\sigma} = d\bar{\sigma}'_s - d\bar{p}_w^w \mathbf{I}. \quad (2.30)$$

We may now write the complete mathematical model (except for initial and boundary conditions) for saturated flow in a deformable porous medium. For the sake of brevity, we shall assume that the flow model has already been written, and we need only to supplement it by the part that deals with the deformation of the solid matrix. We have to add the following 26 scalar variables:

$$\phi, \quad V_{si}, \quad w_i, \quad \sigma_{sij}, \quad \sigma'_{sij}, \quad \varepsilon_{ij}, \quad \varepsilon_{sk},$$

where ε and ε_{sk} represent the strain and the dilatation of the solid matrix, respectively, with

$$\varepsilon_{sk} = \frac{1}{3} \varepsilon_{ii}. \quad (2.31)$$

In the model, we have the following 26 scalar equations:

- **Momentum balance equation for the porous medium.** For example, we may use (2.22), in which $\bar{\sigma} \equiv \sigma$, and $\bar{\rho}\mathbf{F} \equiv \rho_b g \nabla z$, where ρ_b is the bulk density of the porous medium ($= \phi \rho_w + (1 - \phi) \rho_s$).

- **Relationship between total and effective stress, (2.29).**

- **Constitutive relationship, say, for an elastic solid matrix,**

$$\sigma'_s = \mu'_s \nabla \cdot \mathbf{w} \delta + \lambda'_s [\nabla \mathbf{w} + (\nabla \mathbf{w})^T],$$

where μ'_s and λ'_s are the Lamé constants.

- **Mass balance equation for the solid matrix, (2.12).**

- **Relationship between solid velocity and displacement, (2.14).**

- **Relationship between ε_{ij} and \mathbf{w} , written as**

$$\varepsilon = \frac{1}{2} [\nabla \mathbf{w} + (\nabla \mathbf{w})^T],$$

where $(\cdot)^T$ is the transpose of (\cdot) .

- **Definition of dilatation, (2.31).**

2.2.3. Specific storativity

The term on the l.h.s. of (2.8) represents the *mass of water added to a unit volume of porous medium per unit time*. This term can also be written as:

$$\frac{\partial}{\partial t}(\phi\rho_w) = \phi \frac{\partial\rho_w}{\partial t} + \rho_w \frac{\partial\phi}{\partial t}. \tag{2.32}$$

We note the two effects that contribute to the added water mass: the water compressibility, and the porous medium deformability.

In general, the density of water depends on pressure, p_w , solute concentration, c , and temperature, T_w , i.e., $\rho_w = \rho_w(p_w, c, T_w)$. Then,

$$\frac{\partial\rho_w}{\partial t} = \frac{\partial\rho_w}{\partial p_w} \frac{\partial p_w}{\partial t} + \frac{\partial\rho_w}{\partial c} \frac{\partial c}{\partial t} + \frac{\partial\rho_w}{\partial T_w} \frac{\partial T_w}{\partial t}. \tag{2.33}$$

Here, we shall restrict the discussion to compressible fluid, $\rho_w = \rho_w(p_w)$. Then:

$$\frac{\partial\rho_w}{\partial t} = \frac{d\rho_w}{dp_w} \frac{\partial p_w}{\partial t} = \rho_w \beta_w \frac{\partial p_w}{\partial t}, \tag{2.34}$$

where β_w is the *water compressibility* defined by

$$\beta_w = \frac{1}{\rho_w} \frac{d\rho_w}{dp_w}. \tag{2.35}$$

To develop the second term on the r.h.s. of (2.32), let us start from the assumption (already employed before) that the density of the solid, ρ_s , *not of the solid matrix*, remains unchanged as the porosity undergoes changes. Given a fixed mass of solid matrix, m_s , this means that $\partial\mathcal{U}_s/\partial t = 0$, where \mathcal{U}_s denotes the volume of solid,

In the case of *vertical stresses only*, considered above, omitting the overbar symbol for an average, we have

$$\frac{\partial\mathcal{U}_s}{\partial\sigma'_s} = 0, \tag{2.36}$$

where σ'_s is the vertical effective stress. Hence, in view of (2.27), written for the vertical direction only, and assuming no change in the total stress, i.e., $d\sigma = 0$, and $d\sigma'_s = dp_w$, we may write

$$\frac{\partial\mathcal{U}_s}{\partial\sigma'_s} \equiv \frac{\partial}{\partial\sigma'_s}(1 - \phi)\mathcal{U}_{pm} = 0, \tag{2.37}$$

or, with $U_{pm} (= U_s/(1 - \phi))$ denoting the porous medium volume containing U_s ,

$$\frac{1}{U_{pm}} \frac{\partial U_{pm}}{\partial \sigma'_s} = \frac{1}{1 - \phi} \frac{\partial \phi}{\partial \sigma'_s} = \frac{1}{1 - \phi} \frac{\partial \phi}{\partial p_w}. \quad (2.38)$$

At this point, we assume that we deal with relatively small volume changes, and that the soil may be assumed to behave as an *elastic material*. The *coefficient of soil compressibility*, α , is defined for this case of vertical stresses only, as

$$\alpha = \frac{1}{U_{pm}} \frac{\partial U_{pm}}{\partial \sigma'_s} = \frac{1}{1 - \phi} \frac{\partial \phi}{\partial p_w}, \quad (2.39)$$

so that

$$\frac{\partial \phi}{\partial t} = (1 - \phi) \alpha \frac{\partial p_w}{\partial t}. \quad (2.40)$$

The coefficient α can be determined in a laboratory experiment with a *representative volume* of soil of a fixed mass. Sometimes, the soil's compressibility is expressed by a *coefficient of rock compressibility*, α' , such that

$$\phi = \phi_o [1 + \alpha' (p - p_o)],$$

where p_o and ϕ_o are reference values of pressure and porosity, respectively.

By inserting (2.34), and (2.40) into (2.32), we obtain

$$\frac{\partial}{\partial t} (\phi \rho_w) = \rho_w [\phi \beta_w + (1 - \phi) \alpha] \frac{\partial p_w}{\partial t} = S_{op}^{m*} \frac{\partial p_w}{\partial t}. \quad (2.41)$$

In this equation, $S_{op}^{m*} (= \rho_w [\phi \beta_w + (1 - \phi) \alpha])$ can be interpreted as the *specific mass storativity* of a saturated porous medium. It is defined as the mass of water released from (or added to) storage in a unit volume of a deformable porous medium per unit decline (or rise) in water pressure.

By making use of the relationship

$$\frac{\partial h^*}{\partial t} = \frac{1}{\rho_w(p)g} \frac{\partial p_w}{\partial t},$$

we can define a specific storativity with respect to changes in piezometric head (actually, in Hubbert's potential, h^* , defined in (2.2)). Thus, groundwater hydrologists define a *specific storativity*:

$$S_o^* \equiv g S_{op}^{m*} = \rho_w g [\phi \beta_w + (1 - \phi) \alpha], \quad (2.42)$$

as the volume of water released from storage in a unit volume of porous medium, per unit decline in the piezometric head (e.g., [1]). Here,

$$\rho_w S_o^* \frac{\partial h^*}{\partial t} = S_{op}^{m*} \frac{\partial p_w}{\partial t}. \tag{2.43}$$

Although, to simplify the presentation, we have developed the relationship between changes in ϕ and changes in σ'_s (and hence in p_w) by considering only the vertical direction, the same considerations may be extended to a three-dimensional space. For example, Verruijt, [2], showed that, subject to certain simplifying assumptions,

$$\varepsilon_{sk} = \alpha p_w^{ex}, \tag{2.44}$$

where p_w^{ex} is the water pressure in excess of some initial steady state one, and α is the coefficient defined in (2.39).

We may now return to the mass balance (2.8), and insert into it an appropriate expression for the temporal rate of change in $\phi\rho$, i.e., in the mass of water per unit volume of porous medium. For example, by making use of (2.41) and (2.43), the mass balance equation for water in a deformable porous medium can be written in either of the following two forms:

$$S_{op}^{m*} \frac{\partial p_w}{\partial t} = -\nabla \cdot (\rho_w \mathbf{q}_w) + \rho_w \Gamma'^w. \tag{2.45}$$

$$\rho S_o^* \frac{\partial h_w^*}{\partial t} = -\nabla \cdot (\rho_w \mathbf{q}_w) + \rho_w \Gamma'^w, \tag{2.46}$$

in which \mathbf{q}_w ($= \phi \mathbf{V}$) expresses the specific discharge.

We recall that Darcy's law does not express \mathbf{q}_w . Instead, it expresses \mathbf{q}_{rw} . Hence, starting from (2.21), which involves the relative specific discharge, \mathbf{q}_{rw} , the mass balance equation takes the form:

$$\rho_w S_o \frac{\partial h_w^*}{\partial t} = -\nabla \cdot (\rho_w \mathbf{q}_{rw}) + \rho_w \Gamma'^w, \tag{2.47}$$

in which S_o is another specific (volume) storativity, defined by

$$S_o = \rho_w g (\phi \beta_w + \alpha). \tag{2.48}$$

With the above discussion on specific storativity, we may write the mass balance equation for saturated flow in terms of Hubbert's potential, in the form:

$$\rho_w S_o \frac{\partial h_w^*}{\partial t} = -\nabla \cdot (\rho_w \mathbf{q}_{rw}) + \rho_w \Gamma'^w. \tag{2.49}$$

When $|\phi \partial \rho_w / \partial t| \gg |\mathbf{q}_{rw} \cdot \nabla \rho_w|$, and $h^* \approx h$, the last equation reduces to

$$S_o \frac{\partial h_w}{\partial t} = -\nabla \cdot \mathbf{q}_{rw} + \Gamma'^w. \quad (2.50)$$

This equation is the one most commonly used to describe the movement of water under saturated flow conditions. It is based on the assumptions that the fluid is incompressible and the solid is non-deformable, except that the effect of these compressibilities is incorporated in the coefficient of specific storativity. Actually, hydrologists use (2.50), with S_o defined by the r.h.s. of (2.42), and with \mathbf{q}_{rw} replaced by \mathbf{q}_w .

For point sources of strength $P^m(\mathbf{x}, t)$, positive for injection and negative for pumping, the source term in the mass balance equation takes the form:

$$\rho \Gamma' = \rho \sum_m P^m(x^m, y^m, z^m, t) \delta(x - x^m, y - y^m, z - z^m),$$

where $\delta(x - x^m, y - y^m, z - z^m)$ denotes the *Dirac-delta function* at \mathbf{x}^m .

Combined with the motion (= flux) equation, and taking into account the compressibility of the fluid and the solid matrix, the mass balance equation for saturated flow of a compressible fluid, $\rho = \rho(p)$, in a deformable porous medium, takes the form of the *flow equation*:

$$S_{op}^m \frac{\partial p}{\partial t} = \nabla \cdot \left[\rho \frac{\mathbf{k}}{\mu} \cdot (\nabla p + \rho g \nabla z) \right] + \rho \Gamma', \quad (2.51)$$

where \mathbf{k} is the permeability tensor, and

$$S_{op}^m = \rho(\phi\beta + \alpha), \quad \text{with} \quad \beta = \frac{1}{\rho} \frac{d\rho}{dp}, \quad \alpha = -\frac{1}{1-\phi} \frac{\partial(1-\phi)}{\partial p}, \quad (2.52)$$

is the *specific mass storativity*, in which β is the coefficient of compressibility of the fluid, and α is the coefficient of soil compressibility, [2]. The specific mass storativity is defined as the *mass of fluid added per unit volume of porous medium per unit increase in pressure*. The pressure, $p = p(\mathbf{x}, t)$, is the variable for which a solution of (2.51) is sought.

If we assume

$$\left| \phi \frac{\partial \rho}{\partial t} \right| \gg |\mathbf{q}_r \cdot \nabla \rho|, \quad (2.53)$$

i.e., the spatial variability of density is much smaller than the temporal one, (2.51) reduces to

$$S_{op} \frac{\partial p}{\partial t} = \nabla \cdot \left[\frac{\mathbf{k}}{\mu} \cdot (\nabla p + \rho g \nabla z) \right] + \Gamma', \quad (2.54)$$

where the *specific storativity*, S_{op} , is defined by

$$S_{op} = (\phi\beta + \alpha). \tag{2.55}$$

In terms of the piezometric head, h , the *specific (volume) storativity*,

$$S_o (\equiv gS_{op}^m) = \rho g (\phi\beta + \alpha), \tag{2.56}$$

(dims. L^{-1}) is defined as the *volume of water released from (or added to) storage per unit volume of porous medium per unit decline (or rise) the piezometric head*, and the balance equation then takes the form:

$$S_o \frac{\partial h}{\partial t} = \nabla \cdot (\mathbf{K} \cdot \nabla h) + \Gamma'. \tag{2.57}$$

Let us conclude this part of the discussion on the mass balance equation by a comment concerning the definition of specific storativity. We note the difference between the expressions for S_o^* and S_o . This difference is explained by the difference between \mathbf{q}_w and \mathbf{q}_{rw} , appearing in the divergence term in the mass balance equation. Recalling that $\mathbf{q} = \mathbf{q}_r + \phi \mathbf{V}_s$, and expressing the velocity of the solid in terms of solid matrix strain variation (e.g., [5]), leads to (2.51), with the definition of specific storativity with respect to pressure changes presented in (2.52).

In soil mechanics, an *undrained test* (on a saturated soil sample) is one in which water is (practically) stationary relative to the solids, i.e., $\mathbf{q}_{rw} = 0$. Then, any added water goes only into storage in the sample, raising the pressure of the water in the sample. Accordingly, $S_o (= \rho_w(\alpha + \phi\beta_w))$ may be considered as a definition for specific storativity under the conditions equivalent to those prevailing in an undrained test. Thus, S_o is applicable when the coordinate system moves with the solid matrix, while S_o^* is appropriate for a reference frame in which solid and fluids move about freely.

2.3. Initial and boundary conditions

To obtain a unique stable solution of a p.d.e. that describes the mass balance equation in a specified porous medium domain, we have to solve it subject to specified initial and boundary conditions.

Initial conditions specify the value of the dependent variable, e.g., p or h , at all points within the modelled domain at some initial time, usually taken as $t = 0$:

$$p(x, y, z, 0) = f(x, y, z), \quad (2.58)$$

where $f(x, y, z)$ is a known function.

Boundary conditions In principle, there exist two kinds of boundary conditions:

- Continuity in the value of the considered intensive quantity, say, e , across the boundary, expressed in the form of the *no-jump condition*:

$$[[e]]_{1,2} \equiv e|_1 - e|_2 = 0. \quad (2.59)$$

This is a consequence of the continuity in the microscopic value, e , as any microscopic boundary is crossed. A jump in e would lead to an infinite gradient which, in turn, would create an infinite diffusive flux that will instantly eliminate the jump.

- In the absence of sources and sinks on a boundary, the total amount of any considered extensive quantity that is carried by all phases present in the porous medium domain must be conserved as it is being transported across the boundary. This condition arises from the conservation of that quantity as it is transported across a considered boundary.

For the kind of p.d.e.'s considered here, we need a single boundary condition for every boundary segment. Together, the set of specified conditions must satisfy certain compatibility conditions.

Let us review the practical forms of the types of conditions that may be applied to boundary segments of a three-dimensional flow domain. We wish to emphasize that the type of boundary condition to be selected in any particular case depends on the available data concerning the actual or anticipated behavior on the boundary in the field. For the sake of simplicity, we'll express the initial and boundary conditions in terms of h .

- **Prescribed piezometric head on a boundary segment** (e.g., a river, or a lake). The condition is

$$h(x, y, z, t) = f(x, y, z, t), \quad (2.60)$$

where $f(x, y, z, t)$ is a known function.

A boundary condition which specifies the value of a state variable (here, p_w , or h) along a boundary segment is called *boundary condition of the first type*, or *Dirichlet boundary condition*.

• **Prescribed flux normal to a boundary segment.** The boundary surface is a *material surface* with respect to the solid, and, hence,

$$(\mathbf{V}_s - \mathbf{u})|_{inside} \cdot \mathbf{n} = (\mathbf{V}_s - \mathbf{u})|_{outside} \cdot \mathbf{n} = 0, \quad (2.61)$$

where \mathbf{V}_s and \mathbf{u} are the velocities of the solid and of the surface, respectively. The no-jump (i.e., continuity) condition for such a surface takes the form:

$$(\phi \mathbf{V} - \mathbf{u})|_{inside} \cdot \mathbf{n} = (\mathbf{V} - \mathbf{u})|_{outside} \cdot \mathbf{n} = 0, \quad (2.62)$$

where the right hand side represents the *known* flux on the external side of the boundary. With (2.61), the last equation reduces to the form:

$$\mathbf{q}_r|_{inside} \cdot \mathbf{n} = \mathbf{q}_r|_{outside} \cdot \mathbf{n}. \quad (2.63)$$

The specific flux, \mathbf{q}_r , must be known outside. On the inside, it has to be expressed by an appropriate motion equation (e.g., Darcy's law). For an *impervious boundary*, (2.63) reduces to

$$\mathbf{q}_r \cdot \mathbf{n} = 0, \quad (2.64)$$

i.e., the normal component vanishes. We may have *slip* along the boundary.

Consider a non-deformable, stationary porous medium, and let \mathbf{N} denote the *known* prescribed flux on the external side of a boundary, i.e., $\mathbf{q}_r \equiv \mathbf{q}$, and $\mathbf{u} = 0$. The boundary surface is described by $F = F(\mathbf{x})$, with $\mathbf{n} \equiv \nabla F / |\nabla F|$ denoting the outward unit vector normal to it. For a horizontal surface, $\mathbf{n} = \nabla z$. The boundary condition of prescribed flux takes the form:

$$\mathbf{q} \cdot \mathbf{n} = N, \quad N = \mathbf{N} \cdot \mathbf{n}. \quad (2.65)$$

In terms of h , we can write:

$$-(\mathbf{K} \cdot \nabla h) \cdot \mathbf{n} = \mathbf{N} \cdot \mathbf{n}. \quad (2.66)$$

The condition that specifies the gradient of a scalar variable on the boundary is called a *boundary condition of the second kind* or a *Neumann boundary condition*, or a *natural boundary condition*.

• **Semi-pervious boundary** (Fig. 4). This kind of boundary condition occurs when a river or a lake is in contact with an aquifer through a

$p < 0$. Water at a rate \mathbf{N} (= volume of water per unit area per unit time), from precipitation or irrigation, reaches the phreatic surface from above. For vertically downward accretion, $\mathbf{N} = -N\nabla z$. Here, we shall assume that this water accretion has the same quality and density as aquifer water. We have used the term ‘accretion’ to denote the rate at which water is added to, or removed from the phreatic surface, independent of the movement of the latter and of the moisture content (if present) in the void space above it. However, it should be emphasized that $\mathbf{N} \cdot \mathbf{n}$ is not the rate at which water actually it crosses the phreatic surface. This net rate depends on the movement of the phreatic surface. Following the usual procedure, we have to specify both the

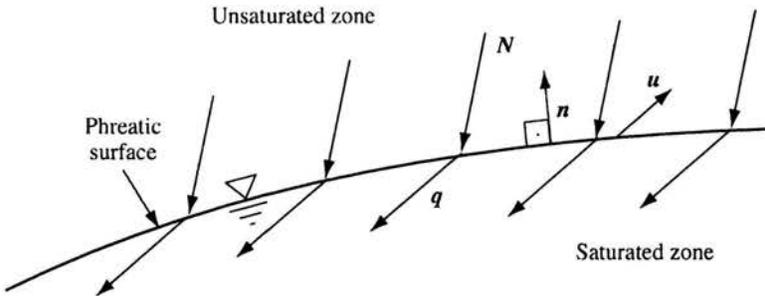


Figure 5: Phreatic surface with accretion.

shape of the boundary surface and the condition to be satisfied on it.

The shape of the phreatic surface, $F(x, y, z, t) = 0$, is, usually, *a-priori* unknown. In fact, in many flow problems, determining the shape and position of this surface is the very objective of the investigations. However, once we have a solution, say, in the form of $p = p(x, y, z, t)$, since on the phreatic surface we *always* have $p(x, y, z, t) = 0$ or $h(x, y, z, t) - z = 0$, the shape of the phreatic surface boundary is given by

$$F(x, y, z, t) \equiv p(x, y, z, t) = 0, \quad \text{or} \quad F(x, y, z, t) \equiv h(x, y, z, t) - z = 0. \tag{2.68}$$

The condition on the phreatic surface boundary is that of continuity of the normal flux component. The underlying assumption is that above this surface, the moisture content is at its *irreducible* level, θ_{rw} . This assumption is valid as long as the thickness of the capillary fringe is small relative to that of the unsaturated zone. If this condition is not satisfied, then this sharp interface (= phreatic surface) approach is not applicable, and we have to consider air-water flow in the unsaturated zone.

With the above assumption, the condition on the phreatic surface is

$$\phi(\mathbf{V} - \mathbf{u})|_{sat\ side} \cdot \mathbf{n} = \theta_{rw}(\mathbf{V} - \mathbf{u})|_{unsat\ side} \cdot \mathbf{n}, \quad (2.69)$$

where \mathbf{V} is the fluid's velocity, \mathbf{u} is the speed of the moving phreatic surface, and $\mathbf{N} = \theta_{rw}\mathbf{V}|_{unsat}$ denotes the rate of accretion reaching that surface.

The rate at which water crosses the phreatic surface into the saturated zone may be expressed in the form:

$$\theta_{rw}(\mathbf{V} - \mathbf{u})|_{unsat} \cdot \mathbf{n} \equiv (\mathbf{N} - \theta_{rw}\mathbf{u})|_{unsat} \cdot \mathbf{n}. \quad (2.70)$$

By inserting the last expression into (2.69), we obtain

$$(\mathbf{q}_w|_{sat} - \mathbf{N}) \cdot \mathbf{n} = (\phi - \theta_{rw})\mathbf{u} \cdot \mathbf{n}. \quad (2.71)$$

Equation (2.71) is the sought boundary condition.

Let us rewrite it in a number of equivalent forms. In view of (1.9) and (1.10), we may rewrite (2.71) as

$$(\mathbf{q}_w|_{sat} - \mathbf{N}) \cdot \nabla F = -(\phi - \theta_{rw}) \frac{\partial F}{\partial t}. \quad (2.72)$$

Making use of (2.68), we may rewrite (2.72) in terms of the piezometric head, h , in the form:

$$(\mathbf{q}|_{sat} - \mathbf{N}) \cdot \nabla(h - z) = -(\phi - \theta_{rw}) \frac{\partial h}{\partial t}. \quad (2.73)$$

By inserting $\mathbf{q} \equiv \mathbf{q}_r = -\mathbf{K} \cdot \nabla h$ into this equation, we obtain

$$(\mathbf{K} \cdot \nabla h + \mathbf{N}) \cdot \nabla(h - z) = \phi_{eff} \frac{\partial h}{\partial t}, \quad (2.74)$$

where $\phi_{eff} \equiv \phi - \theta_{rw}$ is often referred to as the *effective porosity*. As we shall see below, it is, in fact, the *specific yield* of the phreatic aquifer.

• **Seepage face** (Fig. 6). Whenever a phreatic surface approaches a body of open water, a river or a lake, which serves as part of the boundary of the flow domain, it will terminate on that (known) boundary at a point (B) which is higher than the water table of that open water body. The location of that point is *a-priori unknown*. The segment (AB) along the external boundary

of the porous medium, between the water table of that body of open water and the phreatic surface is called the *seepage face*. Along the seepage face, water emerges to the atmosphere.

As the emerging water takes the form of a very thin film flowing along the seepage face, its pressure there is atmospheric, often taken as $p = 0$. Hence, the boundary condition along the seepage face is

$$h(\mathbf{x}, t) = z. \tag{2.75}$$

Thus, the head is specified to be equal to the *known* elevation of each point of the seepage face. The geometry of the seepage face is, thus, known except for the location of its end point, which is also a point on the phreatic surface.

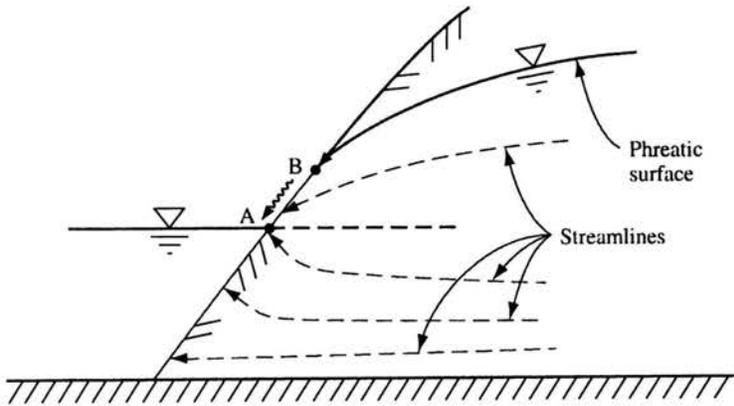


Figure 6: The seepage face, AB.

• **Boundary between different porous media**, e.g., between soil layers. Two conditions have to be specified on such a boundary: continuity of pressure and continuity of normal flux:

$$p|_{side\ 1} = p|_{side\ 2}, \quad \text{or} \quad h|_{side\ 1} = h|_{side\ 2}, \tag{2.76}$$

$$\mathbf{q}_r|_{side\ 1} \cdot \mathbf{n} = \mathbf{q}_r|_{side\ 2} \cdot \mathbf{n}. \tag{2.77}$$

We have, thus, concluded the review of modeling saturated fluid flow in a three-dimensional flow domain. The complete model consists of the mass balance equation, initial conditions, and an appropriate set of boundary conditions. Information is required about coefficients such as the hydraulic conductivity, \mathbf{K} and the specific storativity, S_o .

3. Modeling two-dimensional flow in aquifer domains

This kind of model is very common in groundwater hydrology, where it is used to predict the response of an aquifer to the implementation of various management alternatives.

3.1. Aquifers and essentially horizontal flow

Aquifer is a term used for a porous geological formation that (1) contains water at full saturation (i.e., the entire interconnected void space is filled with water), and (2) permits water to move through it under ordinary field conditions. Thus, whether a geological formation can be referred to as an aquifer, or not, depends on its ability to store and transport water *relative* to other formations in the vicinity.

A *confined* aquifer is one that (1) is bounded from above and from below by impervious formations, and (2) the water pressure in it is such that the level of water in a well that is open (i.e., screened) in it will be at, or will rise above the upper bounding impervious surface.

A *phreatic*, or *unconfined*, *aquifer* is an aquifer that is bounded from above by a *phreatic surface*, or *water table*, assumed to be a sharp surface: saturated zone below it, and zero, or water at residual water saturation above it.

A *leaky phreatic aquifer* is a phreatic aquifer that is bounded from below by a semi-pervious layer, usually referred to as an *aquitard*. This is a layer that is much less pervious than the aquifer overlaying it, and is usually also much thinner. It thus behaves as a *semi-pervious membrane* through which leakage out of or into the phreatic aquifer, from an underlying saturated zone is possible.

A *leaky confined aquifer* is a confined aquifer, except that one or both confining layers are aquitards, through which leakage may take place.

Under certain conditions, flow in an aquifer may be *conceptually* modelled

(albeit *as an approximation*) as taking place in a horizontal planar domain. The transformation of the three-dimensional mathematical model into such a two-dimensional one is performed by integrating (or averaging) the former along the vertical coordinate axis. The term “hydraulic approach” is often used to describe such approximation.

In most regional hydrogeological investigations, the domain of interest in an aquifer is such that *its horizontal extent is much larger than the thickness of the aquifer*. When flow takes place in such a relatively thin domain, which may encompass only a portion of the entire aquifer, the vertical variations in pressure, in piezometric head, or in any other state variable, are often much smaller than the horizontal ones. Under such conditions, it may be useful to employ the hydraulic approach in order to describe the flow in the aquifer in terms of variables that are averaged over the aquifer’s thickness.

Consider, for example, the piezometric head, $h = h(x, y, z, t)$. Its average over the vertical thickness, $B(x, y, t)$, of the flow domain of interest in an aquifer is defined by

$$\bar{h}(x, y, t) = \frac{1}{B(x, y, t)} \int_{B(x, y, t)} h(x, y, z, t) dz. \quad (3.1)$$

The same averaging definition is applicable to other variables and coefficients. In terms of such averaged variables, the flow model is reduced to a two-dimensional one in the horizontal, xy -plane.

In addition to the mathematical advantage achieved by reducing the model from three to two dimensions, a two-dimensional flow model requires less data about the spatial distributions of the various model coefficients.

The assumption of *essentially horizontal flow*, usually referred to as *Dupuit assumption* (1863), is often used to model flow in aquifers. It was first introduced to describe flow in phreatic aquifers. Under the Dupuit assumption, equipotentials are vertical, and, equivalently, the pressure distribution along the vertical is hydrostatic.

In the vicinity of partially penetrating wells, springs, and areas through which an aquifer is drained (e.g., a river, lake, or ocean), the flow is definitely three-dimensional (unless the river or lake fully penetrate the aquifer’s thickness—a very rare situation). Along a groundwater divide (in a three-dimensional flow domain), we definitely have downward flow ([2], p. 82). However, as a rule of thumb, based on theoretical grounds, the essentially horizontal flow approximation is valid beyond a (horizontal) distance of

about twice the thickness of the saturated flow domain from a partially penetrating sink or source of groundwater. This means that when dealing with large horizontal distances in relatively thin aquifers, the approximation of essentially horizontal flow is valid practically everywhere. Indeed, in practice, it is often applied to the entire aquifer, realizing that some error is introduced in the vicinity of partially penetrating sources and sinks and near water divides.

3.2. Averaging over the vertical

Before presenting the equations that describe flow in confined, phreatic and leaky aquifers, let us present the methodology for developing models of flow and transport in horizontal two-dimensional domains from three-dimensional ones. The methodology will be presented in general terms so that we may apply it (obviously, when justified) also to the case of contaminant transport.

The general *macroscopic balance equation* for any extensive property, E , having a (macroscopic) density, e , in saturated flow through an aquifer has the form:

$$\frac{\partial}{\partial t}(\phi e) + \nabla \cdot (e\mathbf{q} + \phi \mathbf{J}_h^E) - \Gamma'' = 0, \quad (3.2)$$

where ϕ denotes the porosity, \mathbf{q} denotes the specific discharge, $\phi \mathbf{J}_h^E$ denotes the sum of dispersive and diffusive fluxes of the considered extensive quantity, per unit area of porous medium, and Γ'' denotes the total rate of production of E , due to both internal production and influx across the (microscopic) surface that bounds the considered phase, per unit volume of porous medium.

According to the methodology of the hydraulic approach, we integrate (3.2) along the vertical thickness, $B(x, y, t)$, of the considered (confined, leaky, or phreatic) aquifer. Let the latter be bounded from below and from above by (possibly moving) surfaces at elevations $z = b_1(x, y, t)$ and $z = b_2(x, y, t)$, respectively, with $b_2 - b_1 = B(x, y, t)$. Another way of expressing the geometry of these boundary surfaces is by the equations (see Subs. 1.6):

$$\begin{aligned} F_1 &\equiv F_1(x, y, z, t) = z - b_1(x, y, t) = 0, \\ F_2 &\equiv F_2(x, y, z, t) = z - b_2(x, y, t) = 0. \end{aligned} \quad (3.3)$$

The two surfaces are shown in Fig. 7.

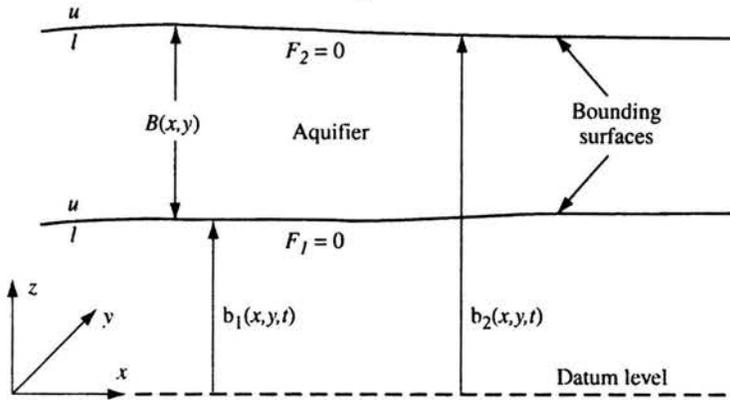


Figure 7: Nomenclature for integration over the thickness of an aquifer.

With the above definitions of the F -surfaces, we have

$$\nabla F_i = \nabla(z - b_i) \quad \text{and} \quad \frac{\partial F_i}{\partial t} = -\frac{\partial b_i}{\partial t}, \quad i = 1, 2.$$

Also, for any surface $F_i = F_i(x, y, z, t)$, we have

$$\frac{\partial F_i}{\partial t} + \mathbf{u} \cdot \nabla F_i = 0, \quad \text{or} \quad \frac{\partial b_i}{\partial t} - \mathbf{u} \cdot \nabla(z - b_i) = 0, \quad i = 1, 2. \quad (3.4)$$

For stationary boundaries,

$$b_i = b_i(x, y), \quad \frac{\partial F_i}{\partial t} = 0, \quad i = 1, 2.$$

By integrating (3.2) along the thickness, B , we obtain:

$$\int_{b_1}^{b_2} \frac{\partial \phi e}{\partial t} dz + \int_{b_1}^{b_2} \nabla \cdot (e\mathbf{q} + \phi \mathbf{J}_h^E) dz - \int_{b_1}^{b_2} \Gamma'' dz = 0. \quad (3.5)$$

Since we have here integrals of derivatives, with integration boundaries that are space- and possibly time-dependent, let us recall two rules for taking integrals of derivatives. These rules are based on *Leibnitz' rule* for a derivative of an integral with respect to a variable upon which the boundaries of the latter depend. We rewrite this rule here in the form:

$$\frac{\partial}{\partial r} \int_{b_1}^{b_2} \mathbf{A} dz = \int_{b_1}^{b_2} \frac{\partial \mathbf{A}}{\partial r} dz + \mathbf{A} \Big|_{b_2} \frac{\partial b_2}{\partial r} - \mathbf{A} \Big|_{b_1} \frac{\partial b_1}{\partial r}, \quad (3.6)$$

where $\mathbf{A} = \mathbf{A}(x, y, z, t)$ is any tensor field, and r stands for x, y , or t .

Using of the average symbol presented in (3.1) for h , we define $\overline{\overline{\mathbf{A}'}}$ as:

$$\overline{\overline{\mathbf{A}'}}(x, y, t) = \frac{1}{B(x, y, t)} \int_{b_1(x, y, t)}^{b_2(x, y, t)} \mathbf{A}(x, y, z, t) dz, \quad (3.7)$$

in which the prime symbol denotes a vector (or vector operator) in the two-dimensional (x, y) plane only, viz.,

$$\mathbf{A}' = A_x \mathbf{1}_x + A_y \mathbf{1}_y, \quad \nabla'(\cdot) = \frac{\partial}{\partial x}(\cdot) \mathbf{1}_x + \frac{\partial}{\partial y}(\cdot) \mathbf{1}_y,$$

where $\mathbf{1}_x$ and $\mathbf{1}_y$ denote unit vectors in the x - and y -directions.

Making use of Leibnitz rule, we may write for any vector, \mathbf{A} :

$$\begin{aligned} \int_{b_1(x, y, t)}^{b_2(x, y, t)} \nabla \cdot \mathbf{A} dz &= \int_{b_1}^{b_2} \left(\nabla' \cdot \mathbf{A}' + \frac{\partial A_z}{\partial z} \right) dz \\ &= \nabla' \cdot \int_{b_1}^{b_2} \mathbf{A}' dz - \mathbf{A}'|_{b_2} \cdot \nabla' b_2 + \mathbf{A}'|_{b_1} \cdot \nabla' b_1 + A_z|_{b_2} - A_z|_{b_1} \\ &= \nabla' \cdot B \overline{\overline{\mathbf{A}'}} + \mathbf{A}|_{b_2} \cdot \nabla(z - b_2) - \mathbf{A}|_{b_1} \cdot \nabla(z - b_1) \\ &= \nabla' \cdot B \overline{\overline{\mathbf{A}'}} + \mathbf{A}|_{F_2} \cdot \nabla F_2 - \mathbf{A}|_{F_1} \cdot \nabla F_1. \end{aligned} \quad (3.8)$$

Here, and henceforth, $|_{F_i}$ stands for $|_{F_i=0}$.

For any scalar, $A(x, y, z, t)$, with $b_1 = b_1(x, y, t)$, $b_2 = b_2(x, y, t)$, we have:

$$\begin{aligned} \int_{b_1}^{b_2} \frac{\partial A}{\partial t} dz &= \frac{\partial}{\partial t} \int_{b_1}^{b_2} A dz - A|_{b_2} \frac{\partial b_2}{\partial t} + A|_{b_1} \frac{\partial b_1}{\partial t} \\ &= \frac{\partial}{\partial t} B \overline{\overline{A}} + A|_{F_2} \frac{\partial F_2}{\partial t} - A|_{F_1} \frac{\partial F_1}{\partial t}. \end{aligned} \quad (3.9)$$

By employing (3.4), (3.5), (3.8), and (3.9), we obtain:

$$\begin{aligned} \frac{\partial}{\partial t} B \overline{\overline{\phi e}} + \nabla' \cdot B \left(\overline{\overline{e \mathbf{q}'}} + \overline{\overline{\phi \mathbf{J}_h^E}} \right) \\ + [\phi e(\mathbf{V} - \mathbf{u}) + \phi \mathbf{J}_h^E]|_{F_2} \cdot \nabla F_2 \\ - [\phi e(\mathbf{V} - \mathbf{u}) + \phi \mathbf{J}_h^E]|_{F_1} \cdot \nabla F_1 - B \overline{\overline{\Gamma^{\prime\prime}}} = 0, \end{aligned} \quad (3.10)$$

in which \mathbf{q}' denotes the specific discharge vector in the horizontal xy -plane. This is the averaged, two-dimensional (in the horizontal plane) balance equation for E in an aquifer. The values of $\overline{e\mathbf{q}'}$, $\overline{\phi\mathbf{J}'_h^E}$, and $\overline{\phi e}$ are functions of x, y, t . The terms:

$$[\phi e(\mathbf{V} - \mathbf{u}) + \phi\mathbf{J}_h^E] \Big|_{F_2} \cdot \nabla F_2 \quad \text{and} \quad [\phi e(\mathbf{V} - \mathbf{u}) + \phi\mathbf{J}_h^E] \Big|_{F_1} \cdot \nabla F_1$$

in (3.10) represent the total flux of E through the (possibly moving) boundaries $F_2 = 0$ and $F_1 = 0$ that bound the aquifer from above and below, respectively. In other words, these terms represent *flux conditions* on these surfaces. We note that while these terms are boundary conditions in the three-dimensional balance equation (3.2), they appear as *source terms* in the averaged, two-dimensional equation (3.10). Our next objective is to consider these conditions for particular cases.

At any point on a boundary $F = 0$, in the absence of sources or sinks of E on the latter, there should be no jump in the normal component of the total flux of that quantity. Using subscripts *ext* and *int* to denote the *external* and *internal* sides of this boundary, respectively, we may rewrite this condition for an extensive quantity that is transferred through the fluid only in the form:

$$\llbracket \phi e(\mathbf{V} - \mathbf{u}) + \phi\mathbf{J}_h^{E_\alpha} \rrbracket_{ext,int} \cdot \mathbf{n} = 0, \tag{3.11}$$

where the symbol $\llbracket (\cdot) \rrbracket$ denotes the jump in (\cdot) from one side (here, external) of the boundary to the other (here, internal).

In what follows, we shall assume that the impervious or semi-pervious top and bottom surfaces that bound an aquifer are material surfaces with respect to the solid's mass. Hence, on these surfaces $(\mathbf{V}_s - \mathbf{u}) \cdot \mathbf{n} = 0$, and, therefore

$$\phi(\mathbf{V} - \mathbf{u}) \cdot \mathbf{n} = \phi(\mathbf{V} - \mathbf{u}) \cdot \mathbf{n} - \phi(\mathbf{V}_s - \mathbf{u}) \cdot \mathbf{n} = \phi(\mathbf{V} - \mathbf{V}_s) \cdot \mathbf{n} \equiv \mathbf{q}_r \cdot \mathbf{n}.$$

Recall that \mathbf{q}_r denotes the specific discharge of the fluid relative to the solid; it is expressed by Darcy's law.

We may now use (3.11) to replace the terms in (3.10) that express the flux conditions on the 'internal sides' of the boundaries by terms that involve (*known*) information on the corresponding 'external sides.'

Let us develop the condition for an upper boundary, $F_2 = 0$, and for the case of the mass of water in saturated flow, i.e., $e = \rho$. The results

can easily be applied to other types of boundaries. For this case, and with $[\rho]_{ext,int} = 0$, equation (3.11) reduces to

$$\mathbf{q}_r|_{ext} \cdot \nabla F_2 = \mathbf{q}_r|_{int} \cdot \nabla F_2. \quad (3.12)$$

For an impervious boundary, $\mathbf{q}_r|_{ext} \cdot \nabla F_2 = \mathbf{q}_r|_{ext} \cdot \mathbf{n} = 0$, so that (3.12) reduces to

$$\mathbf{q}_r|_{int} \cdot \nabla F_2 = 0. \quad (3.13)$$

At a leaky boundary, i.e., a surface through which fluid mass can enter or leave the aquifer at a *known* rate, $\rho \mathbf{q}_{leak}$, the condition is

$$\mathbf{q}_r|_{int} \cdot \nabla F_2 = \mathbf{q}_{leak}|_{ext} \cdot \nabla F_2. \quad (3.14)$$

The term $\mathbf{q}_{leak}|_{ext}$ represents the leakage into (or out of) the aquifer on the *external* side of the latter. It can now be expressed in terms of the state variables of a considered problem.

For a phreatic aquifer with accretion, F_2 represents the water table. The condition on such a boundary takes the form:

$$[\phi \rho (\mathbf{V} - \mathbf{u})]|_{int} \cdot \nabla F_2 = \rho' (\mathbf{N} - \theta_{rw} \mathbf{u})|_{ext} \cdot \nabla F_2, \quad (3.15)$$

or, by rearranging terms, and using (1.9):

$$(\rho' \mathbf{N} - \rho \mathbf{q}) \cdot \nabla F_2 = (\phi \rho - \theta_{rw} \rho') \frac{\partial F_2}{\partial t}. \quad (3.16)$$

Here, \mathbf{N} denotes the rate of accretion of water having a density ρ' , and θ_{rw} denotes the irreducible moisture content assumed to prevail above the phreatic surface.

For downward accretion at a rate N , we introduce $\mathbf{N} = -N \nabla z$, and (3.16) becomes

$$(\rho' N \nabla z + \rho \mathbf{q}) \cdot \nabla F_2 = -(\phi \rho - \theta_{rw} \rho') \frac{\partial F_2}{\partial t}. \quad (3.17)$$

Let us now rewrite the balance equation (3.10), making use of the following approximations:

- The *macrodispersive flux* of the total mass, $\overline{\hat{\rho} \mathbf{q}'}$, due to vertical variations in \mathbf{q}' and in ρ , may be neglected, i.e., $\overline{\rho \mathbf{q}'} = \overline{\rho} \overline{\mathbf{q}'} + \overline{\hat{\rho} \mathbf{q}'} \approx \overline{\rho} \overline{\mathbf{q}'}$, where the symbol $(\hat{\cdot})$ denotes deviation of (\cdot) from its average, $(\overline{\cdot})$.

- The average of the dispersive flux of the total mass is much smaller than the advective mass flux at the averaged level, i.e., $|\overline{\phi \mathbf{J}_h^{m'}}| \ll |\overline{\rho \mathbf{q}}'|$.

A discussion on dispersion and macrodispersion is presented in Sec. 4.

With these approximations, (3.10) can be rewritten in the form:

$$\begin{aligned} \frac{\partial}{\partial t}(B\overline{\phi\rho}) + \nabla' \cdot (B\overline{\rho \mathbf{q}}') + [\rho(\mathbf{q} - \phi\mathbf{u})]_{F_2} \cdot \nabla F_2 \\ - [\rho(\mathbf{q} - \phi\mathbf{u})]_{F_1} \cdot \nabla F_1 - B\overline{\Gamma}'' = 0. \end{aligned} \quad (3.18)$$

For confined and leaky-confined aquifers, $\mathbf{u} \equiv 0$. For a phreatic and a leaky-phreatic aquifer, the lower bounding surface is assumed to be stationary.

Let us now rewrite the last balance equation separately for each type of aquifer, without the averaging symbol, and with the appropriate expression for the flux conditions that take place across the surfaces that bound the aquifer from above and below.

3.3. Averaged aquifer flow equations

3.3.1. Conceptual model

- [A.1] The flow domain is an aquifer, visualized as a relatively thin domain, so that the assumption of *essentially horizontal flow* is justified everywhere within the aquifer. All wells fully penetrate the aquifer, and so are rivers and lakes that act as boundaries also.
- [A.2] The variable is the (vertically averaged) piezometric head, $h = h(\mathbf{x}, t)$.
- [A.3] Water density and viscosity remain constant. In a system of leaky aquifers, the same water density exists in all aquifers.
- [A.4] Spatially distributed natural replenishment, $R = R(x, y, t)$ (= volume of water per unit area per unit time; dims. L/T), having the same density as aquifer water, reaches the water table and replenishes a phreatic aquifer.
- [A.5] The two major properties of a confined aquifer are:
 - * *Aquifer transmissivity*, $\mathbf{T} = \mathbf{T}(x, y)$ (dims. L²/T), which is a product of the average hydraulic conductivity $\mathbf{K} = \mathbf{K}(x, y)$ (dims. L/T) and the aquifer thickness, $B(x, y)$. For an anisotropic aquifer material, \mathbf{T} is a second rank tensor in the xy -plane.

* *Confined aquifer storativity* (due water and solid matrix compressibility), $S(x, y)$ (dimensionless), defined as *volume of water released from (or added to) storage in a unit area of aquifer, per unit decline (or rise) of piezometric head.*

[A.6] For a phreatic aquifer, the two major properties are:

* *Averaged hydraulic conductivity*, $\mathbf{K} = \mathbf{K}(x, y)$.

* *Specific yield, or phreatic aquifer storativity*, $S_y = S_y(x, y)$ (dimensionless) (due mainly to water filling up or draining out of the void space), defined as *volume of water drained out of (or added to) storage in) a unit area of aquifer, per unit decline (or rise) of the water table.* It is assumed that $S_y \ll S_o(h - \eta)$, where S_o is the *specific storativity* (dims. L^{-1}), so that the effect of water and solid matrix compressibility can be neglected. Figure 8 shows the relation between specific yield and grain size.

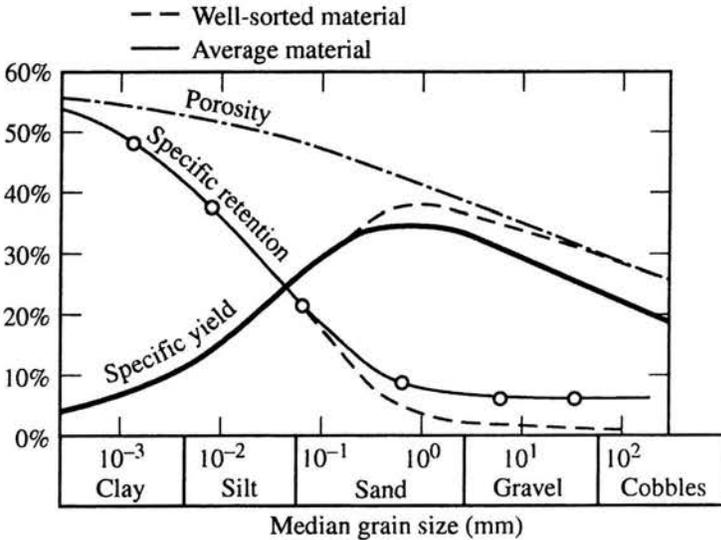


Figure 8: (from Conkling *et al.*, [6], as modified by Davis and DeWiest, [7]).

[A.7]

The flux in a confined (or leaky-confined) aquifer (through the entire aquifer thickness, per unit width), for the case of $\mathbf{K} = \mathbf{K}(x, y)$, is obtained by integration:

$$\begin{aligned}
 \mathbf{Q}' &= \int_{b_1}^{b_2} \mathbf{q} dz = -\mathbf{K} \cdot \int_{b_1}^{b_2} \nabla h dz \\
 &= -\mathbf{K} B \cdot \nabla' \bar{h} - \mathbf{K} \cdot \left[\bar{h} \nabla' B - h(x, y, z = b_2) \nabla' b_2 + h(x, y, z = b_1) \nabla' b_1 \right].
 \end{aligned}
 \tag{3.19}$$

We invoke the *Dupuit assumption*, i.e., that equipotentials can be approximated as vertical, $\bar{h} \approx h(x, y, b_1) \approx h(x, y, b_2)$, so that (3.19) reduces to

$$\mathbf{Q}' = -\mathbf{T} \cdot \nabla' \bar{h} \equiv -\mathbf{T} \cdot \nabla h, \quad \mathbf{T} = \mathbf{K}(x, y) B(x, y), \tag{3.20}$$

where we have used the symbol $h = h(x, y, t)$ to denote $\bar{h}(x, y, t)$.

For $\mathbf{K} = \mathbf{K}(x, y, z)$,

$$\mathbf{T} = \int_{b_1}^{b_2} \mathbf{K} dz = B \bar{\mathbf{K}}'. \tag{3.21}$$

[A.8] The flow in a phreatic (or leaky-phreatic) aquifer (through the entire thickness, per unit width) is expressed by the flux equation:

$$Q'_i = -K_{ij}(h - \eta) \frac{\partial h}{\partial x_j}, \quad i, j = x, y, \tag{3.22}$$

where $\eta = \eta(x, y)$ denotes the elevation of the aquifer's bottom above some datum level, and $h = h(x, y, t)$ denotes the average piezometric head above the same datum level. Often, and here also, the averaged piezometric head is approximated as the elevation of the water table.

[A.9] Pumping and artificial recharge take place through wells. The rate of pumping at a well located at point \mathbf{x}^m is $P^m(\mathbf{x}, t)$ (positive for pumping and negative for artificial recharge).

[A.10] In a leaky aquifer, we often assume (but not always) that (1) there is no change in water storage within the *aquitard* (overlying and/or underlying the aquifer), (2) that the head distribution within the aquitard is linear, and that, therefore, (3) the linear distribution adjusts itself *instantaneously* as the heads in the overlying and underlying aquifers, vary. Then, the (instantaneous) rate of leakage *into* a leaky aquifer is given by:

$$\mathbf{q}_{leak} \Big|_{F_2} \cdot \nabla F_2 = K_\ell \frac{h - h \Big|_{czt}}{B_\ell} |\nabla F_2|, \tag{3.23}$$

where $h|_{ext}$ denotes the piezometric head above the upper or below the lower aquitard, and K_ℓ and B_ℓ denote the hydraulic conductivity and thickness of the aquitard, respectively. The term B_ℓ/K_ℓ is referred to as the *resistance* (dims. T) of the aquitard.

If we wish to take storage in the aquitard into account, we have two options: (1) model the system of aquifers and aquitards as a three-dimensional heterogeneous domain, or (2) construct an approximate model with essential horizontal (2-d) flow in the aquifers, and vertical (1-d) flow in the aquitards. The piezometric heads in the aquifers that overlay and underlie an aquitard will serve as boundary conditions to the flow in the aquitard.

3.3.2. Flow equations

Following are the averaged flow equations, with $h(x, y, t)$ denoting the averaged piezometric head in the aquifer.

- **Confined aquifer.** The flow equation is

$$S \frac{\partial h}{\partial t} = \frac{\partial}{\partial x_i} \left(T_{ij} \frac{\partial h}{\partial x_j} \right) - \sum_{(m)} P^m(x^m, y^m, t) \delta(x - x^m, y - y^m), \quad i, j = 1, 2, \quad (3.24)$$

where $\delta(x - x^m, y - y^m)$ denotes the Dirac-delta function at \mathbf{x} . This equation is often referred to as the *Boussinesq equation*.

- **Phreatic aquifer.** The flow equation is:

$$S_y \frac{\partial h}{\partial t} = \frac{\partial}{\partial x_i} \left(K_{ij} [h - \eta] \frac{\partial h}{\partial x_j} \right) + R(x, y, t) - \sum_{(m)} P^m(x^m, y^m, t) \delta(x - x^m, y - y^m), \quad i, j = 1, 2. \quad (3.25)$$

In (3.25), the product $\mathbf{K}(h - \eta)$ plays the role of transmissivity of a phreatic aquifer. However, here the transmissivity may be time dependent because $h = h(x, y, t)$. As a result, the flow equation for flow in a phreatic aquifer is *nonlinear*.

- **Leaky-confined aquifer.** The flow equation is:

$$S \frac{\partial h}{\partial t} = \frac{\partial}{\partial x_i} \left(T_{ij} \frac{\partial h}{\partial x_j} \right) - \sum_{(m)} P^m(x^m, y^m, t) \delta(x - x^m, y - y^m) + q_{v1} + q_{v2}, \tag{3.26}$$

where q_{v2} and q_{v1} denote leakage *into* the aquifer from above and below, respectively. Note that the two q_v 's involve the piezometric heads in both the considered aquifer and in the ones that overlay and/or underlie it. The piezometric heads in these aquifers have to be known. Otherwise, the flow models for the considered aquifer and for the other two aquifers have to be written and solved simultaneously.

3.3.3. Initial and boundary conditions

To complete the model that describes flow in an aquifer, we need to supplement the flow equation by appropriate initial conditions within the (2-d) domain, and boundary conditions along its boundary. All boundaries are assumed to extend through the entire thickness of the aquifer.

Following are of the kinds of boundary conditions that may be encountered. All conditions are applicable to the three kinds of aquifers. Obviously, in a phreatic aquifer, the phreatic surface is no more a boundary, and the existence of the seepage face is neglected.

- **Boundary of prescribed piezometric head on a boundary segment** (e.g., a river, or a lake). The condition is $h = h(x, y, t) = f(x, y, t)$, where $f(x, y, t)$ is a known function.

- **Boundary of prescribed flux normal to a boundary segment.**

Following the discussion in Subs. 2.3, the boundary condition of this kind takes the form:

$$\mathbf{Q}'|_{inside} \cdot \mathbf{n} = \mathbf{Q}'|_{outside} \cdot \mathbf{n}, \tag{3.27}$$

where the normal unit vector here is in the 2-d plane, and \mathbf{Q}' is expressed by the appropriate flux equation.

For an *impervious boundary*, (3.27) reduces to

$$\mathbf{Q}' \cdot \mathbf{n} = 0. \tag{3.28}$$

Let $\mathbf{W}(x, y, t)$ denote the prescribed flux on the external side of a *stationary* boundary. The prescribed flux condition then takes the form:

$$\mathbf{Q}' \cdot \mathbf{n} = W, \quad W = \mathbf{W} \cdot \mathbf{n}. \quad (3.29)$$

In terms of h , we can write this condition in the form:

$$-(\mathbf{K} \cdot \nabla h) \cdot \mathbf{n} = \mathbf{W} \cdot \mathbf{n}. \quad (3.30)$$

• **Semi-pervious boundary.** Following the discussion in Subs. 2.3, the boundary condition of this kind takes the form:

$$(-\mathbf{K} \cdot \nabla h) \cdot \mathbf{n} = \frac{h - h_{ext}}{c_r}, \quad (3.31)$$

where h_{ext} is the piezometric head on the external side of the semi-pervious “membrane” adjacent to the boundary.

4. Transport of a single contaminant

We consider the case of a single chemical species, a solute or a contaminant, that is being transported in a considered flow domain under isothermal conditions. By solving the flow models discussed so far, we obtain the velocity of the fluid present in that domain. This velocity is required as input information to the contaminant (= solute) transport model.

In general, the flow problem and the contaminant transport one, may be decoupled and solved sequentially. However, when the concentration affects the fluid's density, and/or its viscosity (Sec. 5), the two problems cannot be decoupled. They must be solved simultaneously.

Although in this review we focus on saturated porous media, in this section, we'll occasionally refer also to unsaturated flow, using the symbol θ to denote the volumetric fraction of a fluid phase that occupies part of the void-space. In saturated flow, $\theta = \phi$ (i.e., the porosity).

4.1. Fluxes

4.1.1. Advective flux

Consider the transport of a chemical species (a solute or a contaminant) within a fluid phase that occupies part of the void space (volumetric fraction θ). With $\mathbf{V} \equiv \mathbf{q}/\theta$ (or \mathbf{q}/ϕ in saturated flow) denoting the (intrinsic phase) average (mass weighted) velocity of the phase, and c denoting the (intrinsic phase) average concentration of the contaminant (as mass per unit phase volume), the *advective flux*, \mathbf{J}_{adv} , of the considered chemical species is given by

$$\mathbf{J}_{adv} = \theta \mathbf{V} c. \quad (4.1)$$

This flux expresses the mass of the chemical species passing through a unit area of porous medium, normal to \mathbf{V} , per unit time.

4.1.2. Diffusive flux

We visualize a multi-component fluid phase as consisting of a number of components, each made up of a large number of identical molecules (ions, atoms, etc) that are in constant random motion. Each molecule has mass, momentum, and energy.

Each extensive quantity of a chemical species, or of a phase, present in a given domain, may be regarded as a continuum at the microscopic level. The behavior of this microscopic continuum is obtained by averaging the behavior of the molecules that comprise it. The behavior at the macroscopic level is obtained by averaging the behavior of the microscopic continuum.

The *microscopic flux*, \mathbf{j}^E , of an extensive quantity, E , and \mathbf{j}^{E^γ} , of the extensive quantity, E^γ , can be expressed as

$$\mathbf{j}^E = e\mathbf{V}^E, \quad \mathbf{j}^{E^\gamma} = e^\gamma\mathbf{V}^{E^\gamma}, \quad (4.2)$$

with

$$\mathbf{j}^E = \sum_{(\gamma)} \mathbf{j}^{E^\gamma} = \sum_{(\gamma)} e^\gamma \mathbf{V}^{E^\gamma}, \quad (4.3)$$

where e denotes the density of E , and $e = \sum_{(\gamma)} e^\gamma$. In these equations, the velocities, \mathbf{V}^E of a particle of an E -continuum of a phase, and \mathbf{V}^{E^γ} of a particle of an E^γ -continuum of a γ -component of a phase, are defined as

$$\mathbf{V}^E = \left. \frac{\partial \mathbf{x}^E}{\partial t} \right|_{\boldsymbol{\xi}^E = \text{const.}}, \quad \mathbf{V}^{E^\gamma} = \left. \frac{\partial \mathbf{x}^{E^\gamma}}{\partial t} \right|_{\boldsymbol{\xi}^{E^\gamma} = \text{const.}}, \quad (4.4)$$

where \mathbf{x}^E denotes the position vector of the E -particle, the material coordinates of which are expressed by $\boldsymbol{\xi}^E$.

Physically, $e\mathbf{V}^E$ represents the quantity of E passing through a unit area of the continuum normal to the direction of \mathbf{V}^E , per unit time.

The same flux may also be expressed as the sum

$$e\mathbf{V}^E = e\mathbf{V} + e(\mathbf{V}^E - \mathbf{V}) \equiv e\mathbf{V} + \mathbf{j}^E. \quad (4.5)$$

We have, thus, decomposed the (total) flux of E into two parts:

- An *advective E -flux*, $e\mathbf{V}$, carried by the mass-weighted velocity of the phase, with respect to a fixed coordinate system.

- A flux, $e(\mathbf{V}^E - \mathbf{V})$, relative to the advective one. This second flux, denoted by \mathbf{j}^E , is called the *diffusive flux of E* (relative to the mass weighted velocity):

$$\mathbf{j}^E = e(\mathbf{V}^E - \mathbf{V}). \quad (4.6)$$

We may now apply the above definitions to the particular case in which E is the mass of a γ -component of a fluid phase, with $e \equiv \rho^\gamma$.

For a γ -component of a phase, the mass flux is expressed by $\rho^\gamma \mathbf{V}^\gamma$. When decomposed into two parts, we obtain:

$$\rho^\gamma \mathbf{V}^\gamma = \rho^\gamma \mathbf{V} + \rho^\gamma (\mathbf{V}^\gamma - \mathbf{V}) = \rho^\gamma \mathbf{V} + \mathbf{j}^\gamma, \quad (4.7)$$

where:

$$\mathbf{j}^\gamma = \rho^\gamma (\mathbf{V}^\gamma - \mathbf{V}) \quad (4.8)$$

is the *diffusive mass flux* of the γ -component, usually referred to as *molecular diffusion*. We note that for all (N) components within a phase:

$$\sum_{\gamma=1}^N \rho^\gamma (\mathbf{V}^\gamma - \mathbf{V}) = \sum_{\gamma=1}^N \rho (\mathbf{V}^\gamma - \mathbf{V}) = 0.$$

We have decomposed the total mass flux of a γ -component into two parts:

- An *advective mass flux*, $\rho^\gamma \mathbf{V}$, carried by the mass-weighted velocity of the phase, with respect to a fixed coordinate system.
- A *diffusive flux*, $\rho^\gamma (\mathbf{V}^\gamma - \mathbf{V})$, relative to the advective one.

Both fluxes are in terms of mass of component per unit area of fluid phase.

Still at the microscopic level, the flux of molecular diffusion, \mathbf{j}^γ , relative to the advective mass flux of the fluid phase moving at the mass weighted velocity, \mathbf{V} , is expressed by *Fick's law* of molecular diffusion, the form:

$$\mathbf{j}^\gamma = c^\gamma (\mathbf{V}^\gamma - \mathbf{V}) = -\rho \mathcal{D}^\gamma \nabla \omega^\gamma, \quad \sum_{\gamma} \mathbf{j}^\gamma = 0, \quad (4.9)$$

where c^γ ($\equiv \rho^\gamma$) is the concentration (= mass of γ per unit volume of fluid) of the γ -component in the fluid, $\omega^\gamma = \rho^\gamma / \rho$ denotes the mass fraction of γ , and \mathcal{D}^γ (a scalar) is the coefficient of molecular diffusion of a γ -component in a fluid phase. This form of Fick's law expresses the flux of a single component in a fluid that is a *binary system*, i.e., is composed of two components only: a *solute* and a *solvent*. In (4.9), it is assumed that \mathcal{D}^γ is independent of c^γ .

Actually, the diffusive mass flux of a γ -component is driven by the spatial non-uniformity in the *chemical potential* (e.g., Denbigh, 1891), $\mu^\gamma = \mu^\gamma(p, \omega^\gamma, T)$. Thus, the diffusive mass flux takes the form:

$$\mathbf{j}^\gamma = -\mathcal{D}^{\gamma} \nabla \mu^\gamma. \quad (4.10)$$

Usually, the direction of $\nabla \mu^\gamma$ coincides with that of ∇c^γ . Here, the discussion is limited to isothermal conditions.

We note that for a constant fluid density, and this is the case more commonly encountered in practice, (4.9) reduces to:

$$\mathbf{j}^\gamma = c^\gamma (\mathbf{V}^\gamma - \mathbf{V}) = -\mathcal{D}^\gamma \nabla c^\gamma. \quad (4.11)$$

So far, the discussion focused on diffusion at the microscopic level. By averaging (4.9) for a fluid of constant density and constant coefficient of molecular diffusion, over an REV, we obtain an expression for the macroscopic form of Fick's law of molecular diffusion. It expresses the macroscopic diffusive flux, \mathbf{J}^γ , of a γ -component within a fluid phase that occupies the entire void space, or part of it, in the form:

$$\mathbf{J}^\gamma = -\mathcal{D}^\gamma \mathbf{T}^*(\theta) \cdot \nabla c^\gamma = -\mathcal{D}^{*\gamma}(\theta) \cdot \nabla c^\gamma, \quad (4.12)$$

where c^γ is now the component's concentration at the macroscopic level, θ denotes the volumetric fraction of the considered phase, and $\mathcal{D}^{*\gamma} = \mathcal{D}^{*\gamma}(\theta)$ ($= \mathcal{D}^\gamma \mathbf{T}^*(\theta)$), a second rank symmetric tensor, is the *coefficient of molecular diffusion within a phase in a porous medium*. In saturated flow, we replace θ by ϕ .

The second rank tensor \mathbf{T}^* represents the *tortuosity* of the considered fluid phase occupying part of the void space. In an isotropic porous medium, the components, T_{ij}^* , of the tortuosity tensor, can be represented as $T^* \delta_{ij}$, in which T^* is a scalar tortuosity, and δ_{ij} is the ij th component of the *Kronecker delta*, with $\delta_{ij} = 1$ for $i = j$, and $\delta_{ij} = 0$ for $i \neq j$.

For a fluid of variable density, the macroscopic diffusive flux is:

$$\mathbf{J}^\gamma = -\rho \mathcal{D}^{*\gamma}(\theta) \cdot \nabla \omega^\gamma, \quad (4.13)$$

where all variables and the coefficient are at the macroscopic level. Note that all \mathbf{J} -fluxes are *per unit area of fluid* in the porous medium cross-section.

The tortuosity of a phase, which is a second rank symmetric tensor, is a macroscopic geometrical coefficient that expresses the effects on the diffusive flux of the microscopic surface that bounds that phase. As such, it depends on the configuration of the phase within the void space. Hence, in unsaturated flow, each of the tortuosity components is a function of the saturation. In an isotropic porous medium, some authors relate the tortuosity to the volumetric fraction of the phase, in the form, [13]:

$$T^*(\theta) = \frac{\theta^{\frac{7}{3}}}{\phi^2}. \quad (4.14)$$

Because the value of the tortuosity falls in the range zero to unity, the value of diffusivity a porous medium is smaller than the corresponding value in an open fluid body.

4.1.3. *Hydrodynamic dispersion*

The fluid velocity at the microscopic level varies in magnitude and direction from point to point within a fluid present in the void space. As a consequence, any initial cloud of close tracer particles will spread out, gradually changing its shape and the fluid volume occupied by it. This phenomenon is referred to as *mechanical dispersion*.

An additional phenomenon that takes place in the void space, due to concentration gradients, is the *molecular diffusion* discussed above. Even when the macroscopic effect of diffusion is relatively small, it is only the combination of microscopic velocity variations and molecular diffusion that produces mechanical dispersion. Also, it is molecular diffusion which makes the phenomenon of dispersion in purely laminar flow *irreversible*.

We refer to the flux that causes mechanical dispersion (of a component) as *dispersive flux*. It is a *macroscopic* flux that expresses the effect of the microscopic variations of velocity and concentration in the vicinity of a considered point. We note that the decomposition of the average of the total (local) advective flux into an advective flux at the average velocity and a dispersive flux, is a consequence of the selected averaging process.

We use the term *hydrodynamic dispersion* to denote the spreading (at the macroscopic level) that results from both mechanical dispersion and molecular diffusion. Actually, the separation between the two processes is rather artificial, as they are inseparable. However, molecular diffusion alone

does take place in the absence of motion (both in a porous medium and in a fluid continuum). Because molecular diffusion depends on time, its effect on the overall dispersion is more significant at low velocities.

4.1.4. Dispersive flux

The advective flux of a component (per unit area of fluid) at a microscopic point, \mathbf{x}' , within a fluid phase that occupies part of the void space within an REV centered at a point \mathbf{x} , is given by $c\mathbf{V}$. The intrinsic phase average of this flux is $\overline{c\mathbf{V}^f}$. In order to express this flux in terms of the (intrinsic) average values, \overline{c}^f and $\overline{\mathbf{V}}^f$, the velocity, $\mathbf{V}(\mathbf{x}', t; \mathbf{x})$, and the component concentration, $c(\mathbf{x}', t; \mathbf{x})$, are decomposed into two parts: an intrinsic phase average value and a deviation from that value, in the form:

$$\begin{aligned}\mathbf{V}(\mathbf{x}', t; \mathbf{x}) &= \overline{\mathbf{V}}^f(\mathbf{x}, t) + \overset{\circ}{\mathbf{V}}(\mathbf{x}', t; \mathbf{x}), \\ c(\mathbf{x}', t; \mathbf{x}) &= \overline{c}^f(\mathbf{x}, t) + \overset{\circ}{c}(\mathbf{x}', t; \mathbf{x}),\end{aligned}\quad (4.15)$$

with

$$\overline{\overset{\circ}{\mathbf{V}}}^f = 0, \quad \text{and} \quad \overline{\overset{\circ}{c}}^f = 0.$$

To obtain the average flux, still per unit area of fluid, we write

$$\overline{c\mathbf{V}^f} = \overline{(\overline{c}^f + \overset{\circ}{c})(\overline{\mathbf{V}}^f + \overset{\circ}{\mathbf{V}})^f} = \overline{\overline{c}^f \overline{\mathbf{V}}^f} + \overline{\overline{c}^f \overset{\circ}{\mathbf{V}}^f} + \overline{\overset{\circ}{c} \overline{\mathbf{V}}^f} + \overline{\overset{\circ}{c} \overset{\circ}{\mathbf{V}}^f}. \quad (4.16)$$

Because the average of the deviations vanishes by definition, the second and third terms on the r.h.s. of (4.16) vanish, leaving the relationship

$$\overline{c\mathbf{V}^f} = \overline{c}^f \overline{\mathbf{V}}^f + \overline{\overset{\circ}{c} \overset{\circ}{\mathbf{V}}^f}. \quad (4.17)$$

From this equation it follows that the average (= macroscopic) flux of a component at a point in a porous medium domain is equal to the sum of two macroscopic fluxes:

- An **advective flux**, $\overline{c}^f \overline{\mathbf{V}}^f$, expressing the flux carried by the fluid at the latter's average velocity, $\overline{\mathbf{V}}^f$. This flux was introduced above.
- A flux, $\mathbf{J}^{*\gamma} \equiv \overline{\overset{\circ}{c} \overset{\circ}{\mathbf{V}}^f}$ that results from the variation of c and \mathbf{V} within the REV for which the considered point serves as a centroid. This is the flux that produces the mechanical spreading (\equiv the dispersion) of the component. We refer to it as the *dispersive flux*.

The dispersive flux of a component (per unit area of fluid) in a porous medium is expressed as a *Fickian-type* law, in the form:

$$\mathbf{J}^* \equiv \overline{c\mathbf{V}^f} = -\mathbf{D} \cdot \nabla \overline{c^f}, \tag{4.18}$$

where \mathbf{D} , a second rank symmetrical tensor, with components D_{ij} , is the *coefficient of advective (or mechanical) dispersion*.

The components D_{ij} (dims. L^2/T) of \mathbf{D} are related to the property of the porous medium to disperse a component, to the velocity of the fluid, and to molecular diffusion, by

$$D_{ij} = a_{ijkl} \frac{\overline{V_k^f} \overline{V_l^f}}{\overline{V^f}} f(\text{Pe}, r), \tag{4.19}$$

where $\overline{V^f}$ ($\equiv |\overline{\mathbf{V}^f}|$) is the magnitude of the average velocity, and Pe is a *Peclet number*, defined by

$$\text{Pe} = \frac{\overline{V^f} \Delta_f}{\mathcal{D}_f}, \tag{4.20}$$

which expresses the ratio between the rates of transport of the γ -component by advection and by diffusion. In this definition, Δ_f is the hydraulic radius of the fluid occupied portion of the void space, serving as a characteristic length of the void space, and \mathcal{D}_f denotes the coefficient of molecular diffusion in the fluid phase. In practice, we assume $f(\text{Pe}, r) \approx 1$.

The coefficients a_{ijkl} appearing in (4.19), are components of a 4th rank tensor, \mathbf{a} , called the *dispersivity* of the porous medium (dims. L). It expresses the effect of the microscopic configuration of the solid-fluid interface. When an α -fluid occupies only part of the void space, each of the dispersivity components, a_{ijkl} , reflecting the geometry of α -fluid within an REV, depends on the volumetric fraction, θ_α .

As stated above, the coefficient of dispersion, \mathbf{D} , is a symmetrical second rank tensor, i.e.,

$$D_{ij} = D_{ji}, \quad i, j = 1, 2, 3.$$

As such, it has *three principal directions*. Using these principal directions as Cartesian coordinate axes, x_1, x_2, x_3 , we may write

$$\mathbf{D} = \begin{bmatrix} D_{x_1x_1} & O & O \\ O & D_{x_2x_2} & O \\ O & O & D_{x_3x_3} \end{bmatrix}. \tag{4.21}$$

However, unlike the second rank tensor of permeability, which is a property *only* of the microscopic configuration of the considered phase inside the void space, the tensor \mathbf{D} (and this means also its principal directions) depends also on the (macroscopic) velocity field. Specifically, if we consider a point on a macroscopic (instantaneous) streamline in a flow domain, we may construct at that point:

- A unit vector, $\boldsymbol{\tau}$, the direction of the *tangent* to the streamline, (i.e., the direction of the flow).
- A unit vector, $\boldsymbol{\nu}$, called the *principal normal* to the streamline. We have $d\boldsymbol{\tau}/ds = \kappa\boldsymbol{\nu}$, where s is the distance measured along the streamline, and κ is the curvature of the streamline at the point.
- A unit vector, $\boldsymbol{\beta}$ ($= \boldsymbol{\tau} \times \boldsymbol{\nu}$), which is normal to both $\boldsymbol{\tau}$ and $\boldsymbol{\nu}$.

In an *isotropic porous medium*, the principal directions of the tensor \mathbf{D} coincide with the directions of these three unit vectors. As such, as the velocity varies, these directions may also vary from point to point and time.

If, *locally*, we select $\boldsymbol{\tau}$, $\boldsymbol{\nu}$ and $\boldsymbol{\beta}$, as *base vectors* of the coordinate system, x_1, x_2, x_3 , then \mathbf{D} takes the form (4.21). In such a case, $D_{x_1x_1}$ is called *coefficient of longitudinal dispersion*, while $D_{x_2x_2}$ and $D_{x_3x_3}$ are called *coefficients of transversal dispersion*.

The dispersivity, \mathbf{a} , is a *fourth rank tensor* that has 81 a_{ijkl} -components in a three-dimensional space. However, because of various symmetry considerations, all but 36 components are zeros. In an *isotropic porous medium*, only 21 non-zero components remain. They, in turn, depend only on *two* parameters: a_L and a_T , called the *longitudinal* and the *transversal dispersivities of the porous medium*, respectively. Both have a length dimension that characterizes the microscopic configuration of the phase within the REV. Thus, for a fluid that completely fills the void space in a granular porous medium, a_L should be of the order of magnitude of a pore size. Laboratory column experiments have shown that a_T is 8 to 24 times smaller than a_L .

For an *isotropic porous medium*, we may express the components of the dispersivity tensor terms of a_L and a_T , in the form:

$$a_{ijkl} = a_T \delta_{ij} \delta_{kl} + \frac{a_L - a_T}{2} (\delta_{ik} \delta_{lj} + \delta_{il} \delta_{jk}). \quad (4.22)$$

The coefficient of dispersion is then expressed by

$$D_{ij} = a_T V \delta_{ij} + (a_L - a_T) \frac{V_i V_j}{V}, \quad (4.23)$$

where δ_{ij} is the ij th component of the *Kronecker delta*.

In Cartesian coordinates, with velocity components V_x , V_y and V_z , we obtain from (4.23)

$$\begin{aligned} D_{xx} &= a_T V + (a_L - a_T) \frac{V_x^2}{V} = \frac{a_T (V_y^2 + V_z^2) + a_L V_x^2}{V}, \\ D_{xy} &= \frac{(a_L - a_T) V_x V_y}{V} = D_{yx}, \\ D_{xz} &= \frac{(a_L - a_T) V_x V_z}{V} = D_{zx}, \\ D_{yy} &= a_T V + \frac{(a_L - a_T) V_y^2}{V} = \frac{a_T (V_x^2 + V_z^2) + a_L V_y^2}{V}, \\ D_{yz} &= \frac{(a_L - a_T) V_y V_z}{V} = D_{zy}, \\ D_{zz} &= a_T V + \frac{(a_L - a_T) V_z^2}{V} = \frac{a_T (V_x^2 + V_y^2) + a_L V_z^2}{V}. \end{aligned} \quad (4.24)$$

4.1.5. Total flux

We may now combine the three modes of component transport—advection, dispersion, and diffusion—and write the total macroscopic flux (per unit area of a fluid f -phase), $\mathbf{J}^{t\gamma}$, in the form:

$$\begin{aligned} \mathbf{J}^{t\gamma} &= \bar{c}^f \bar{\mathbf{V}}^f + \mathbf{J}^\gamma + \mathbf{J}^{*\gamma} \\ &= \bar{c}^f \bar{\mathbf{V}}^f - \mathbf{D}_h^\gamma \cdot \nabla \bar{c}^f, \end{aligned} \quad (4.25)$$

where:

$$\mathbf{D}_h^\gamma \equiv \mathbf{D} + \mathcal{D}^{*\gamma} \quad (4.26)$$

denotes the *coefficient of hydrodynamic dispersion* of the component.

Henceforth, we shall omit the symbol that denotes the intrinsic phase average, as we shall be discussing phenomena only at the macroscopic level.

4.2. Mass balance equation for a contaminant

4.2.1. The general equation

We consider the case of a γ -component (= chemical species, or a contaminant) in a fluid phase (liquid or gas) that occupies the entire void space, or part of it, at a fluid content θ . For saturated flow, we replace θ by ϕ . Since we are considering here only a single chemical species, the superscript γ will be omitted wherever possible.

The macroscopic differential mass balance equation for a component of a fluid phase is obtained by averaging the microscopic mass balance equation for the mass of the component, or directly from the averaged equation (1.6), with appropriate substitutions. With c replacing \bar{c}^α , denoting the average concentration of the component in the fluid-phase, \mathbf{V} replacing $\bar{\mathbf{V}}^\alpha$, denoting the average fluid (mass weighted) velocity, \mathbf{J}^* replacing $\bar{\mathbf{j}}^{\mathbf{E}\alpha}$, denoting the dispersive flux of the component, \mathbf{J}_{diff} replacing $\bar{\mathbf{j}}^{\mathbf{E}\alpha}$, denoting the macroscopic diffusive flux of the component, and $\rho\Gamma$, replacing $\bar{\rho}\Gamma^{\mathbf{E}\alpha}$, denoting the source of mass of the component per unit volume of the considered fluid phase, we rewrite (1.6) in the form:

$$\frac{\partial(\theta c)}{\partial t} = -\nabla \cdot \theta (c\mathbf{V} + \mathbf{J}^* + \mathbf{J}_{diff}) - f_{\alpha \rightarrow \beta} + \theta \rho \Gamma, \quad (4.27)$$

where $f_{\alpha \rightarrow \beta}$ replaces the surface integral term that denotes the rate of transfer of the component from the interior of the considered fluid α -phase to all other (β) phases across the surface that separates the former from the latter *within the REV*. This surface may include both fluid-fluid and fluid-solid portions. In the case of saturated flow, it is comprised only of a fluid-solid surface, and we have $(\mathbf{V} - \mathbf{u}) \cdot \mathbf{n} \equiv 0$. In (4.27), with $\theta (c\mathbf{V} + \mathbf{J}^* + \mathbf{J}_{diff})$, we have:

θc	Mass of the component per unit volume of porous medium.
$\partial(\theta c)/\partial t$	Rate of increase of θc .
$\theta \mathbf{J}_{tot}$	Total flux (= $\theta (c\mathbf{V} + \mathbf{J}^* + \mathbf{J}_{diff})$) of the component, per unit area of porous medium (advection, dispersion and diffusion).
$-\nabla \cdot \theta \mathbf{J}_{tot}$	Excess of inflow over outflow of the component per unit volume of porous medium, per unit time.
$f_{\alpha \rightarrow \beta}$	Rate of transfer of the component from the interior of the α -phase to all β -phases, per unit volume of porous medium.
$\theta \rho \Gamma$	Rate of production of the component, per unit volume of porous medium.

The interphase mass transfer, expressed by $f_{\alpha \rightarrow \beta}$, may be due to a number of processes: adsorption (from a liquid phase to a solid), evaporation or volatilization (i.e., a liquid-gas transfer), dissolution (e.g., solid-liquid transfer), and liquid-liquid transfer. Some of these processes may occur simultaneously. We shall then replace $f_{\alpha \rightarrow \beta}$ by $\sum_{(j)} f_{\alpha \rightarrow \beta, j}$, where j indicates the j th process.

We may regard (4.27) as a single equation in three unknowns: c , $f_{\alpha \rightarrow \beta}$, and Γ . Our primary interest is to solve (4.27) for $c = c(\mathbf{x}, t)$ within a specified porous medium domain. We need an expression for $f_{\alpha \rightarrow \beta}$, in terms of c , or in terms of c_α and c_β (= concentration of the considered component in the α and β phases. We also need information on the source term, Γ .

The nature of $f_{\alpha \rightarrow \beta}$ depends on the process that causes the interphase transfer: adsorption, liquid-liquid diffusive transfer, volatilization, dissolution, etc. It also depends on whether we assume that *equilibrium* conditions prevail, or not. We assume that no sink or source of the mass of the considered component exists on the microscopic interphase boundary. Therefore, the condition of *no-jump* in the normal flux of the component across the boundary prevails at every point on the latter ($f_{\alpha \rightarrow \beta} = -f_{\beta \rightarrow \alpha}$).

- **Under equilibrium conditions.** By writing the mass balance equation for a considered component for every phase present in the system, and adding these equations, we obtain a single mass balance equation for the component *in the porous medium as a whole*. No transfer term appears in this equation, since $\sum_{(\alpha')} f_{\alpha \rightarrow \beta \neq \alpha} = 0$, where α' denotes all phases, including the solid.

However, in this single balance equation we have all the c_α 's as variables, and additional equations are required. We shall see later how various equilibrium (partitioning) relationships among these variables are introduced in order to enable a solution.

- **Under non-equilibrium conditions.** Nothing will be gained by summing up the phase equations to obtain a mass balance equation for the porous medium as a whole. Therefore, we leave the balance equations for the individual phases, and introduce expressions for the rates of interphase mass transfers.

The last term on the r.h.s. of (4.27) also expresses a source (= rate of production)—this time as a consequence of processes that occur *inside* the considered phase. Examples are: chemical reactions, that destroy or produce

the considered component, and radioactive (and other) decay phenomena. As will be explained below, we include here also the source (or sink) due to pumping (or injection) of the considered component from (or into) an aquifer. The various source terms have to be expressed in terms of the concentrations of the chemical species involved in the considered processes. When a number of sources of different kinds are active simultaneously, we replace the last term on the r.h.s. of (4.27) by a sum of similar terms, representing the production of the component by the various source processes.

An important consequence of the above discussion is that one of the first decisions that have to be made when constructing the conceptual model of a problem that involves chemical reactions, is whether the reactions are such that equilibrium may be assumed to prevail, or not. The subject of chemical reactions is not included in this presentation.

Let us elaborate on the various source terms that appear in the component's mass balance equation. We shall first discuss 'homogeneous reactions' (i.e., Γ -type sources), and then 'heterogeneous reactions', i.e., f -type ones.

4.2.2. Pumping and injection

The term $\theta\rho\Gamma$ in (4.27) denotes a source that occurs within the fluid. The symbolic expression $\Gamma = \Gamma(\mathbf{x}, t)$ may refer to both distributed and point sources. In both cases, the source term expresses the rate at which the considered component is added to the porous medium per unit volume of the latter. It is a source when the component is being produced in the domain. A sink is a negative source. By pumping, the component is removed from the domain at the concentration prevailing at the sink's location at the time of withdrawal.

Let a fluid phase (liquid or gas) containing a considered component at a known concentration c_R , be added as a distributed external fluid source, at the rate $R_{ext} = R_{ext}(\mathbf{x}, t)$ (= volume of fluid added per unit volume of porous medium per unit time). Then, the source term appearing (4.27) is expressed by

$$\theta\rho\Gamma^y = R_{ext}(\mathbf{x}, t)c_R. \quad (4.28)$$

In this (symbolic) form, $R_{ext}(\mathbf{x}, t)$ represents a *distributed source*.

When sources exist at N isolated points, $\mathbf{x}^{(m)}$, $m = 1, 2, \dots, N$, the source

term in (4.27) takes the form:

$$\theta\rho\Gamma^\gamma = \sum_{(m)} R_{ext}^{(m)}(\mathbf{x}^{(m)}, t)\delta(\mathbf{x} - \mathbf{x}^{(m)})c_R^{(m)}, \tag{4.29}$$

where $R_{ext}^{(m)}$ represents the rate of injection (in terms of volume added per unit time) at point $\mathbf{x}^{(m)}$ at time t , of fluid at the *known* concentration $c_R^{(m)}$, and $\delta(\mathbf{x} - \mathbf{x}^{(m)})$ denotes the *Dirac delta function*.

For a distributed sink and for point sinks (e.g., pumping wells), the corresponding expressions are, respectively:

$$\theta\rho\Gamma^\gamma = Q_{ext}(\mathbf{x}, t)c(\mathbf{x}, t), \tag{4.30}$$

and

$$\theta\rho\Gamma^\gamma = \sum_{(r)} Q_{ext}^{(r)}(\mathbf{x}^{(r)}, t)\delta(\mathbf{x} - \mathbf{x}^{(r)})c(\mathbf{x}, t), \tag{4.31}$$

where the withdrawn fluid is at the *unknown concentration*, $c(\mathbf{x}, t)$.

4.2.3. Decay and other degradation phenomena

For radioactive decay, the source term takes the form:

$$\theta\rho\Gamma = -\theta\lambda c,$$

in which λ is the *first order rate constant* of the radioactive decay. For an adsorbed component that undergoes radioactive decay, the source term takes the form:

$$\Gamma_s = -\lambda F,$$

where F denotes the *mass of component per unit mass of solid*. If we assume that adsorption follows a *linear isotherm* (see next subsection), the last expression is replaced by

$$\Gamma_s = -\lambda K_d c.$$

For any other decay or degradation phenomena of a considered component, the source term takes the form:

$$\theta\rho\Gamma = -\theta k_f c,$$

where k_f represents the *degradation rate constant* for the component in the fluid phase. For an adsorbed component, we have

$$\Gamma_s = -k_s F,$$

where k_s represents the *degradation rate constant* for the adsorbate.

4.2.4. Adsorption

Adsorption (the opposite of *desorption*) is the phenomenon of accumulation of a chemical species present in a liquid (*adsorbate*) that occupies the void space, or part of it, on the solid matrix (*adsorbent*) at the liquid-solid interface. It is caused by the attraction of the species to the surfaces of the solid, or by reactions of one or more species in the fluid with the solid.

Let us assume that adsorption is the only interphase transfer mechanism ($\beta = s$). In such a case, the term $f_{\alpha \rightarrow \beta}$ appearing in (4.27) takes the form:

$$f_{\alpha \rightarrow s} \equiv f_{\alpha \rightarrow s} = \rho_b \left. \frac{dF}{dt} \right|_{\text{ads}},$$

where $\rho_b (= (1 - \phi)\rho_s)$ denotes the *bulk density of the solid matrix*. However, this rate is unknown. Equation (4.27) contains the unknowns: c and $f_{\alpha \rightarrow s}$.

Let us assume that the considered adsorption process is sufficiently fast, so that *chemical equilibrium* may be assumed to prevail. This assumption will enable us to make use of the thermodynamic relationship, called *isotherm*, that expresses the partitioning of the considered component between the solid and the liquid phases.

The equilibrium assumption enables us eliminate the rate of interphase exchange due to adsorption, by writing and summing up the balance equations for the considered component in the fluid phase and on the solid. We need, therefore, the macroscopic balance equation for the considered component *on the solid phase*. We obtain this equation from (4.27), in which the α subscript is replaced by s , θ is replaced by $1 - \phi$, and θc is replaced by $\theta_s \rho_s F (= \rho_b F)$. We assume that no flux of the considered component, whether advective, dispersive, or diffusive, takes place within the solid phase and/or on its surface, i.e., $\mathbf{V} \equiv \mathbf{V}_s = 0$, $\mathbf{J}_s^* = 0$, $\mathbf{J}_{diff,s} = 0$. The resulting mass balance for the component on the solid surface, takes the form:

$$\frac{\partial(\rho_b F)}{\partial t} = -f_{s \rightarrow \alpha} + \rho_b \Gamma_s^\gamma, \quad (4.32)$$

where $\rho_b \Gamma_s$ is the rate of production of the component's mass on the solid surface, per unit volume of porous medium (e.g., due to production or decay process), and $f_{s \rightarrow \alpha} (= -f_{\alpha \rightarrow s})$ expresses the quantity of the component leaving the solid surface, per unit volume of porous medium, due to desorption.

By summing up the two balance equations for the considered component: (4.27) for the component in the fluid and (4.32) for the component on the solid, we obtain the *mass balance equation for the component in the porous medium as a whole*, in the form:

$$\frac{\partial(\theta c + \rho_b F)}{\partial t} = -\nabla \cdot \theta(c\mathbf{V} - \mathbf{D} \cdot \nabla c - \mathcal{D}^* \cdot \nabla c) + \theta \rho \Gamma + \rho_b \Gamma_s. \quad (4.33)$$

When, in addition, the considered component (1) is being withdrawn from a number of pumping wells, (2) is being injected at known concentrations a number of injection wells, and (3) undergoes both radioactive decay, and first order decay, with different rate constants for the component in the fluid and on the solid, (4.33) takes the form:

$$\begin{aligned} \frac{\partial(\theta c + \rho_b F)}{\partial t} = & - \nabla \cdot \theta(c\mathbf{V} - \mathbf{D} \cdot \nabla c - \mathcal{D}^* \cdot \nabla c) \\ & - \rho_b(k_s + \lambda)F - \theta(k_f + \lambda)c \\ & + \sum_{(m)} R_{ext}^{(m)}(\mathbf{x}^{(m)}, t) \delta(\mathbf{x} - \mathbf{x}^{(m)}) c_R^{(m)}(\mathbf{x}^{(m)}, t) \\ & - \sum_{(r)} Q_{ext}^{(r)}(\mathbf{x}^{(r)}, t) \delta(\mathbf{x} - \mathbf{x}^{(r)}) c(\mathbf{x}, t), \end{aligned} \quad (4.34)$$

in which $R_{ext}^{(m)}$ represents the rate of injection (in terms of volume added per unit time) at point $\mathbf{x}^{(m)}$ at time t , of liquid at the *known* concentration, $c_R^{(m)}$, $Q_{ext}^{(r)}$, represents the rate of extraction, e.g., by pumping (in terms of volume extracted per unit time), of liquid at concentration $c(\mathbf{x}, t)$, and $\delta(\mathbf{x} - \mathbf{x}^{(m)})$ denotes the *Dirac delta function*. We have, thus, included also radioactive and first order decay rates.

Equation (4.33) contains the two variables, $c(\mathbf{x}, t)$ and $F(\mathbf{x}, t)$. Hence, *assuming equilibrium conditions*, we now make use of an appropriate *isotherm* that gives the relationship between c and F . For example, we may use the linear *Freundlich isotherm*,

$$F = K_d c, \quad (4.35)$$

and obtain from (4.33) the mass balance equation for the component in the porous medium as a whole, in the form:

$$\begin{aligned} \frac{\partial}{\partial t} (\theta + \rho_b K_d) c \equiv \frac{\partial}{\partial t} \theta R_d c = & -\nabla \cdot \theta(c\mathbf{V} - \mathbf{D} \cdot \nabla c - \mathcal{D}^* \cdot \nabla c) \\ & + \theta \rho \Gamma^\gamma + \rho_b \Gamma_s^\gamma, \end{aligned} \quad (4.36)$$

where

$$R_d = 1 + \rho_b K_d / \theta \quad (4.37)$$

is the *retardation coefficient*. The choice of this name is explained below.

This equation involves only the single variable $c(\mathbf{x}, t)$, expressing the concentration of the considered component in the liquid phase. There is no difficulty in rewriting this equation in terms of concentration of the component in the porous medium as a whole, $c_{pm}^\gamma (= (\theta + \rho_b K_d) c)$.

Once c and F are known, we can determine the sought (instantaneous) rate of transfer from the fluid-phase to the solid, using the relationship

$$f_{\alpha \rightarrow s} = \frac{\partial(\rho_b F)}{\partial t} - \rho_b \Gamma_s. \quad (4.38)$$

When equilibrium cannot be assumed, we have to express the rate of transfer in *both balance equations* in terms of an appropriate rate transfer expression. Typically, this expression has the form $f_{\alpha \rightarrow s} = f(c, F)$, e.g.,

$$f_{\alpha \rightarrow \beta} = \alpha^*(Ac_\alpha - BF), \quad (4.39)$$

where A and B are two coefficients. For example, we may write the model in the form:

$$\begin{aligned} \frac{\partial(\theta c)}{\partial t} &= -\nabla \cdot \theta (c\mathbf{V} + \mathbf{J}^* + \mathbf{J}_{diff}) + f_{s \rightarrow \alpha} + \theta \rho \Gamma, \\ \frac{\partial(\rho_b F)}{\partial t} &= -f_{s \rightarrow \alpha} + \rho_b \Gamma_s, \\ f_{s \rightarrow \alpha} &= k'_f c - k'_r F. \end{aligned}$$

The three equations have to be solved simultaneously for c , F , and $f_{s \rightarrow \alpha}$.

4.2.5. Mass balance of a component with two-site adsorption

Various authors suggested models that are often referred to as *two-site kinetic* ones. In such a model, the underlying assumption is that the total number of *sorption sites* on the solid surface is made up of two parts: on one, a fraction p of the total surface area, adsorption is assumed to be *instantaneous*, so that equilibrium is always assumed to prevail, while on the other, a fraction $1-p$ of the total area, kinetic conditions prevail, so that adsorption is assumed to be time dependent. Thus,

$$F = F_{eq} + F_{kin}, \quad (4.40)$$

where F_{eq} and F_{kin} represent the mass of adsorbate on sites of the first and of the second types, respectively, per unit mass of solid. We shall assume that for the first type of sites, the linear equilibrium isotherm is applicable, viz.,

$$F_{eq} = pK_d c. \tag{4.41}$$

For sites of the second type—the kinetic, non-equilibrium sites—we use the linear reversible rate equation,

$$\left. \frac{dF_{kin}}{dt} \right|_{ads} = k_{13} [(1 - p)K_d c - F_{kin}], \tag{4.42}$$

in which k_{13} is a *first-order rate coefficient*.

Another two-site model is obtained by writing the rate equation:

$$\left. \frac{dF_{kin}}{dt} \right|_{ads} = k_{14} c - k_{15} F_{kin} = k_{16} \frac{\phi}{(1 - \phi)\rho_s} c - k_{15} F_{kin}, \tag{4.43}$$

in which k_{16} and k_{15} (dims. T^{-1}) are adsorption and desorption rate coefficients, respectively.

Using the isotherm (4.41) to describe equilibrium adsorption, the balance equation (4.33) takes the form:

$$\begin{aligned} \frac{\partial}{\partial t} (\theta + p\rho_b K_d) c &= -\nabla \cdot \theta (c\mathbf{V} - \mathbf{D} \cdot \nabla c - \mathcal{D}^* \cdot \nabla c) - \left. \frac{dF_{kin}}{dt} \right|_{ads} \\ &\quad + \theta \rho \Gamma + \rho_b \Gamma_s, \end{aligned} \tag{4.44}$$

in which $(dF_{kin}/dt)|_{ads}$ is expressed by an appropriate rate transfer expression, say,

$$\left. \frac{dF_{kin}}{dt} \right|_{ads} = k_{13} [(1 - p)K_d c - F_{kin}]. \tag{4.45}$$

The mass balance equation for the component on the solid can be rewritten as:

$$\frac{\partial}{\partial t} (p\rho_b K_d c + \rho_b F_{kin}) = \left. \frac{dF_{kin}}{dt} \right|_{ads} + \rho_b \Gamma_s^{\gamma}. \tag{4.46}$$

Equations (4.44), (4.46), and (4.45) have now to be solved simultaneously for c , F_{kin} , and $dF_{kin}/dt|_{ads}$.

4.2.6. Retardation

The retardation factor, R_d , has already been mentioned above. Let us elaborate on the interpretation of this coefficient.

We consider the case of a liquid that occupies the entire void space, i.e., $\theta = \phi$. We shall assume that: (a) no external sources or sinks exist, (b) $\rho_s = \text{constant}$, and $\partial\phi/\partial t = 0$, i.e., a non-deformable solid matrix, (c) no degradation or decay phenomena take place, and (d) the considered component adsorbs to the solid under conditions of equilibrium, following a linear isotherm, with $\partial K_d/\partial t = 0$. Then, (4.36) reduces to the form:

$$R_d\phi\frac{\partial c}{\partial t} = -\nabla\cdot\phi(c\mathbf{V} - \mathbf{D}\cdot\nabla c - \mathcal{D}^*\cdot\nabla c), \quad (4.47)$$

where:

$$R_d = 1 + \frac{\rho_b K_d}{\phi} \quad (> 1) \quad (4.48)$$

is the *retardation factor*.

To understand the significance of R_d , and the reason for interpreting it as a 'retardation factor', let us further simplify (4.47) by assuming that the porous medium is homogeneous, i.e., $\nabla R_d = 0$. Then, (4.47) may be rewritten as

$$\phi\frac{\partial c}{\partial t} = -\nabla\cdot\phi\left(c\frac{\mathbf{V}}{R_d} - \frac{\mathbf{D}_h}{R_d}\cdot\nabla c\right), \quad (4.49)$$

where $\mathbf{D}_h (= \mathbf{D} + \mathcal{D}^*)$ denotes the coefficient of hydrodynamic dispersion.

For comparison, we refer to the same case, but without adsorption, i.e., $K_d = 0$. For such a case, the balance equation (4.49) takes the form:

$$\phi\frac{\partial c}{\partial t} = -\nabla\cdot\phi(c\mathbf{V} - \mathbf{D}_h\cdot\nabla c). \quad (4.50)$$

We note that (4.49) and (4.50) are similar, except that in the former equation, the average fluid velocity *seems to be* \mathbf{V}/R_d and the coefficient of hydrodynamic dispersion seems to be reduced to \mathbf{D}_h/R_d . We recall that (except when velocities are very low) the major component of \mathbf{D}_h is the coefficient of mechanical dispersion, \mathbf{D} , which is proportional to \mathbf{V} . Thus, under the assumption of equilibrium adsorption, described by a linear isotherm, the effect of adsorption is to *retard* the advance of the component (as part of it is adsorbed to the solid). Instead of advancing with the fluid,

moving at a velocity V , the mean movement of the contaminant is at the reduced, or retarded velocity, V/R_d . At the same time, spreading occurs as if the coefficient of mechanical dispersion, D , is also reduced by the factor R_d , along with the coefficient of molecular diffusion in a porous medium, D^* .

Figure 9 shows the effect of retardation in the example of a semi-infinite column. The curves were obtained by an analytical solution. We note that in the case with adsorption, the point $c = 0.5$ advances at a speed V/R_d , and that the curve is steeper, indicating a smaller coefficient of hydrodynamic dispersion.

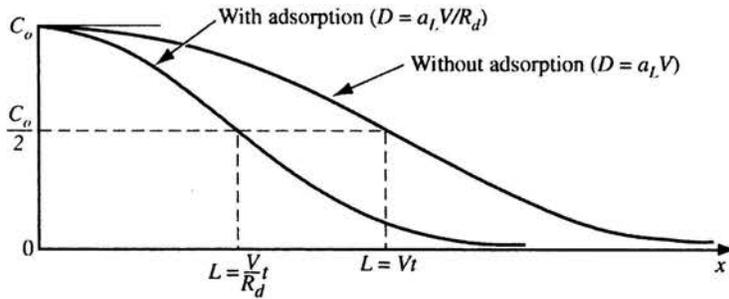


Figure 9: Effect of retardation.

In order to explain the phenomenon of retardation, we have reduced (4.33) to the simpler form (4.49). However, this phenomenon exists also in the more general case, which may include a variety of source terms, although in the absence of equilibrium between F and c , the form (4.49) cannot be obtained.

In unsaturated flow, with a contaminant that is partitioned between the liquid phase and the solid according to the linear isotherm (4.35), the retardation factor takes the form:

$$R_d(\theta) = 1 + \frac{\rho_b K_d}{\theta}, \tag{4.51}$$

which now depends on $\theta(x, t)$. By employing the isotherm (4.35), with the same K_d as in the case of saturated flow, we have assumed that, due to the thin film of water (= the wetting-phase) which covers the solid in the air filled portion of the void space, the entire surface area of the solid provides sites for adsorption. Otherwise, K_d would be a function of the volumetric fraction, i.e., $K_d = K_d(\theta)$.

4.2.7. Mass balance for a volatile component

Although these lectures focus on saturated flow, we have included the discussion on a volatile chemical species, because *volatile organic compounds* (VOC's) are often encountered as contaminants in the unsaturated zone.

We consider the unsaturated zone, with two fluid phases: a gas, g , and a liquid, ℓ , that together occupy the entire void space (at saturations S_g , and S_ℓ , respectively). We recall that the saturation of a fluid phase is defined as the ratio of the volume of the phase per unit volume of the void space. Let the considered contaminant be a VOC that is present only as a vapor component (denoted as superscript v) in the gas; no 'free product' (i.e., liquid VOC) is present in the void space. Thus, the VOC is present in the gaseous phase at a concentration c_g^v , in the aqueous liquid at concentration c_ℓ^v , and as an adsorbate on the solid at concentration F^v . We shall assume that *chemical equilibrium* prevails among all phases, and that the partitioning between the liquid and the solid surface obeys the linear isotherm, $F^v = K_d c_\ell^v$. The partitioning between the gas and the liquid is assumed to obey *Henry's law*:

$$\mathcal{H} \equiv \mathcal{H}_{g,\ell}^v = \frac{c_g^v}{c_\ell^v}. \quad (4.52)$$

We assume that the considered component may undergo first order decay, with rate coefficients λ_g , λ_ℓ and λ_s , in the gas, liquid, and solid phases, respectively. We shall assume that no sources and sinks are present in the considered domain, except that gas is extracted from the void space at a volumetric rate Q_g (= volume of gas per unit volume of porous medium). The solid matrix is assumed to be rigid and stationary. We shall disregard the presence of water vapor as a component in the gas, and of dissolved air as a component in the liquid. Thus, the gas contains 'dry air' (a) and VOC vapor (v), and the liquid contains 'pure water' and dissolved VOC.

Since we are dealing with a single component, we shall henceforth omit the superscript v that denotes it.

Our objective is to write the balance equations that describe the spatial and temporal concentration distributions of the VOC in the two fluid phases and on the solid, i.e., $c_\ell(\mathbf{x}, t)$, $c_g(\mathbf{x}, t)$, and $F(\mathbf{x}, t)$.

The balance equation for the mass of VOC in the gaseous phase, takes

the form:

$$\frac{\partial}{\partial t}(\phi S_g c_g) = -\nabla \cdot \phi S_g (c_g \mathbf{V}_g - \mathbf{D}_{gh} \cdot \nabla c_g) - f_{g \rightarrow \ell} - \lambda_g \phi S_g c_g - Q_g c_g, \quad (4.53)$$

where the symbols $f_{g \rightarrow \ell}$ ($= -f_{\ell \rightarrow g}$) denotes the rate (= mass per unit volume of porous medium) at which VOC is transferred from the gaseous phase to the liquid one, across their (microscopic) common interface.

The balance equation for the mass of VOC in the liquid is

$$\frac{\partial}{\partial t}(\phi S_\ell c_\ell) = -\nabla \cdot \phi S_\ell (c_\ell \mathbf{V}_\ell - \mathbf{D}_{\ell h} \cdot \nabla c_\ell) + f_{g \rightarrow \ell} + f_{s \rightarrow \ell} - \lambda_\ell \phi S_\ell c_\ell, \quad (4.54)$$

with $f_{\ell \rightarrow s}$ denoting the rate of transfer of the contaminant from the liquid to the solid.

The balance equation for the mass of VOC on the solid is

$$\frac{\partial}{\partial t}(\rho_b F) = -f_{s \rightarrow \ell} - \lambda_s \rho_b F, \quad (4.55)$$

where we assume that the entire surface area of the solid is in contact with the liquid (= the wetting fluid), although the liquid in the larger pores is only in the form of thin water films.

We have here three balance equations in five variables: c_ℓ , c_g , F , $f_{g \rightarrow \ell}$, and $f_{s \rightarrow \ell}$. Since equilibrium is assumed for both adsorption and volatilization, we may follow the methodology presented above, of eliminating the rates of transfer. First, we eliminate the rates of transfer between the three phases by summing up the three balance equations. We obtain a single balance equation for the mass of the component in the porous medium as a whole:

$$\begin{aligned} \frac{\partial}{\partial t} [\phi (S_\ell c_\ell + S_g c_g + \rho_b F)] \\ = -\nabla \cdot \phi [S_\ell (c_\ell \mathbf{V}_\ell - \mathbf{D}_{\ell h} \cdot \nabla c_\ell) + S_g (c_g \mathbf{V}_g - \mathbf{D}_{gh} \cdot \nabla c_g)] \\ - \lambda_g \phi S_g c_g, -\lambda_\ell \phi S_\ell c_\ell - \lambda_s \rho_b F - Q_g c_g. \end{aligned} \quad (4.56)$$

At this stage, we have a single equation in three variables. Based on the assumption of equilibrium that underlies this model, we now introduce the information about the partitioning of the VOC among the three phases. Selecting c_ℓ as the variable of the problem, and assuming the domain to

be homogeneous with respect to K_d and Henry's coefficient, $\mathcal{H}(\equiv \mathcal{H}_{g,\ell})$, we obtain:

$$\begin{aligned} \frac{\partial}{\partial t} \left[\phi \left(S_\ell + S_g \mathcal{H} + \frac{\rho_b K_d}{\phi} \right) c_\ell \right] \\ = -\nabla \cdot \phi [\mathcal{H} S_g (c_\ell \mathbf{V}_g - \mathbf{D}_{gh} \cdot \nabla c_\ell) + S_\ell (c_\ell \mathbf{V}_\ell - \mathbf{D}_{\ell h} \cdot \nabla c_\ell)] \\ - \phi \left(\lambda_\ell S_\ell + \lambda_g S_g \mathcal{H} + \frac{\lambda_s \rho_b K_d}{\phi} \right) c_\ell - Q_g \mathcal{H} c_\ell. \end{aligned} \quad (4.57)$$

We recall that the complete model should include also a part that describes the mass transport (= flow) of the two phases. Its solution will provide information on phase velocities, \mathbf{V}_ℓ , \mathbf{V}_g , and on phase saturations, S_ℓ , S_g , that appear in the component balance equation, (4.57).

Whenever equilibrium partitioning may not be assumed, we have to represent the rate of component transfer from one phase to the other by an appropriate rate transfer expression, written in terms of the concentrations of the involved phases. This comment is valid both for the liquid-solid transfer, as well as for the liquid-gas transfer of the considered component.

4.3. Initial and boundary conditions

The solution of any of the balance equations for the mass of a contaminant, requires initial and boundary conditions. Initial conditions involve the specification of the value of the concentration, $c = c(\mathbf{x}, 0)$ at all points \mathbf{x} of the domain at some initial time, say $t = 0$.

4.3.1. General boundary conditions

Following the discussion in Subs. 4.3, here also, the boundary conditions for the contaminant transport models are based on the following two principles:

- At every point on a boundary, there exists no discontinuity in the (intrinsic phase average) concentration, viz.,

$$[c]_{1,2} = 0, \quad (4.58)$$

where $[(\cdot)]_{1,2} \equiv (\cdot)|_1 - (\cdot)|_2$ denotes the jump (\cdot) from side 1 to side 2 of the boundary. For example, sides 1 and 2 may represent the internal side and the external one, respectively.

However, under certain conditions that are consequences of the various assumptions that underlie the problem, we are forced to violate this condition in order to achieve a better approximation of a real situation.

- In the absence of sources and sinks of the considered contaminant on the boundary, which is the usual case, the component normal to the boundary of the total flux of that contaminant, with respect to the (possibly moving) boundary, undergoes no jump as the latter is crossed. With θ denoting the volumetric fraction of the phase, \mathbf{n} denoting the unit vector normal to the boundary, \mathbf{u} denoting the velocity of the latter, this statement takes the form:

$$\llbracket \theta [c(\mathbf{V} - \mathbf{u}) - \mathbf{D}_h \cdot \nabla c] \rrbracket_{1,2} \cdot \mathbf{n} = 0. \tag{4.59}$$

Since we have assumed that the boundary is material with respect to the solid matrix, we may rewrite (4.59) in the form:

$$\llbracket c\mathbf{q}_r - \theta \mathbf{D}_h \cdot \nabla c \rrbracket_{1,2} \cdot \mathbf{n} = 0, \tag{4.60}$$

where \mathbf{q}_r (= specific discharge relative to the solid) is expressed by Darcy's law.

For (4.58) or (4.59) to serve as a condition for c on a boundary, information (on c and/or ∇c) on what happens on the external side of the latter *must be known* as a function of space and time.

4.3.2. Particular cases

We shall assume that all boundaries are stationary, except the phreatic surface. When necessary, subscripts 1 and 2 will be used to denote the internal and external sides of a boundary surface, respectively.

- **Boundary of prescribed concentration.** When the value of $c(\mathbf{x}, t)$ is prescribed as a known function at all points of a boundary segment, due to phenomena that take place on the external side of the that segment, independent of what happens within the domain, the boundary condition is

$$c(\mathbf{x}, t) = f^{(1)}(\mathbf{x}, t), \tag{4.61}$$

where $c(\mathbf{x}, t)$ denotes the the concentration on the internal side of the boundary, while $f^{(1)}(\mathbf{x}, t)$, a known function, represents c on the external side. This is a first kind or *Dirichlet* boundary condition.

• **Boundary of prescribed flux.** When phenomena occurring on the external side of a boundary impose a known total flux of the considered component, say, $f^{(2)}(\mathbf{x}, t)$, normal to a boundary segment, at all points of the latter, regardless of what happens within the considered domain itself, the condition takes the form:

$$(c\mathbf{q}_r - \theta\mathbf{D}_h \cdot \nabla c) \cdot \mathbf{n} = f^{(2)}(\mathbf{x}, t), \quad (4.62)$$

where \mathbf{q}_r can be expressed by one of the motion equations. For saturated flow, θ is replaced by the porosity, ϕ . Since both c and ∇c are involved in (4.62), this is a *Cauchy* or *boundary condition of the second kind*.

On an *impervious boundary* $f^{(2)}(\mathbf{x}, t) = 0$, and $\mathbf{q}_r \cdot \mathbf{n} = 0$, so that (4.62) reduces to

$$(\mathbf{D}_h \cdot \nabla c) \cdot \mathbf{n} = 0. \quad (4.63)$$

This is a *Neumann* or *second kind boundary condition*.

For an impervious boundary surface that coincides with the vertical xz -plane, with $V_y = 0, V_x, V_z \neq 0, n_y = 1, n_x = n_z = 0, D_{hyx} = D_{hyz} = 0, D_{hyy} = a_T V + \mathcal{D}^*$, the condition (4.63), of zero total flux normal to an impervious boundary, reduces to

$$(a_T V + \mathcal{D}^*) \frac{\partial c}{\partial y} = 0, \quad \text{or} \quad \frac{\partial c}{\partial y} = 0. \quad (4.64)$$

• **Boundary between two porous media.** Along such a boundary, we assume the existence of discontinuities in all solid matrix characteristics, e.g., ϕ, k_{ij}, a_{ijkl} , etc. The partial differential (balance) equations cannot be solved for domains with discontinuities in the coefficients. To overcome this difficulty, we divide the problem domain along the surfaces of discontinuity into sub-domains in each of which no such discontinuity exists. Each side serves as the external side to the other one. We then write and solve a complete model for each of these sub-domain. Such a model requires that conditions be specified also along the surface of discontinuity (which now serves as a boundary to both sub-domains): one condition for each side (= sub-domain), for a total of two conditions. Neither the concentration nor the flux are a-priori known on the boundary.

The first condition is that of no-jump in component concentration:

$$c|_1(\mathbf{x}, t) = c|_2(\mathbf{x}, t). \quad (4.65)$$

The second condition is that of continuity in the normal component of the total flux of the considered component:

$$(c\mathbf{q}_r - \theta\mathbf{D}_h \cdot \nabla c)|_1 \cdot \mathbf{n} = (c\mathbf{q}_r - \theta\mathbf{D}_h \cdot \nabla c)|_2 \cdot \mathbf{n}. \tag{4.66}$$

Since $q_r|_1 \cdot \mathbf{n} = q_r|_2 \cdot \mathbf{n}$, and $c|_1 = c|_2$, the last equation reduces to

$$(\theta\mathbf{D}_h \cdot \nabla c)|_1 \cdot \mathbf{n} = (\theta\mathbf{D}_h \cdot \nabla c)|_2 \cdot \mathbf{n}. \tag{4.67}$$

Because both conditions involve the variables of the two adjacent subdomains, the two models are coupled, and have to be solved simultaneously.

• **Boundary with a body of fluid.** We consider a stationary boundary between a porous medium domain (denoted by subscript *pm*) and a body of fluid (denoted by subscript *fb*), assumed to be a ‘well mixed’ domain, i.e., at a *known* uniform concentration of the considered component. A large lake and a river may serve as examples. For the gaseous phase in the soil, the atmospheric air above ground surface may serve as another example.

To simplify the discussion, we consider a saturated porous medium domain in good hydraulic contact with a ‘well mixed’ body of fluid which contains the considered component at a known uniform concentration, c'' .

The condition of no-jump in the normal component of the total flux of the considered component, takes the form:

$$(c''\mathbf{V})|_{fb} \cdot \mathbf{n} - (c\mathbf{q}_r + \phi\mathbf{J}_{diff} + \phi\mathbf{J}^*)|_{pm} \cdot \mathbf{n} = 0, \tag{4.68}$$

where $\phi|_{fb} = 1$. Equation (4.68) expresses the continuity of the mass flux across the boundary of the component in the water, by advection, diffusion and dispersion. Since the fluid body is assumed to be at a uniform concentration, only advection takes place in it. The use of \mathbf{q}_r stems from the assumption that the boundary is material with respect to the solid matrix. When $\mathbf{V}_s = 0$, we have $\mathbf{q}_r \equiv \mathbf{q}$.

Expressing the dispersive and diffusive fluxes in terms of ∇c , we may rewrite (4.68) the form:

$$(c\mathbf{V})|_{fb} \cdot \mathbf{n} - (c\mathbf{q}_r - \phi\mathbf{D}_h \cdot \nabla c)|_{pm} \cdot \mathbf{n} = 0. \tag{4.69}$$

Consequently, when no advection takes place across the boundary, $\mathbf{V}|_{fb} \cdot \mathbf{n} = \mathbf{q}_r \cdot \mathbf{n} = 0$, the dispersive flux $\mathbf{J}^* = 0$, and (4.69) reduces to

$$(\mathcal{D}^* \cdot \nabla c)|_{pm} \cdot \mathbf{n} = 0. \tag{4.70}$$

This implies that no transport of mass by molecular diffusion takes place across such a boundary, even when $c|_{pm} \neq c''$. This conclusion is unacceptable. Under the physical conditions of this example, we should expect transport of the component to take place between the porous medium domain and the adjacent fluid body by molecular diffusion, as this remains the only possible mode of transport.

The error in the conclusion expressed by (4.70) stems from the assumption that a 'well mixed' zone exists on the external side of the boundary. This assumption, in the absence of advection, combined with the sharp boundary approximation, must yield no mass flux by diffusion across it. In order to reinstate the diffusive-dispersive flux, which does take place in reality, we introduce the concept of a *transition zone*, *boundary layer*, or *buffer zone*, of width δ at the boundary. Instead of the boundary between the body of fluid and the porous medium, we now consider the boundary between the latter and the transition zone. Assuming that the sum of dispersive and diffusive fluxes through the transition zone is proportional to the average concentration gradient, and that the latter is proportional to the concentration difference $c - c''$, we express the condition of continuity of flux at the boundary by

$$c'' \mathbf{V}|_{fb} \cdot \mathbf{n} - \alpha^*(c - c'') = (c\mathbf{q}_r - \phi \mathbf{D}_h \cdot \nabla c)|_{pm} \cdot \mathbf{n}, \quad (4.71)$$

where α^* is a *transfer coefficient*, such that $\alpha^*(c'' - c)$ represents the sum of diffusive and dispersive fluxes through the transition zone.

Since, $\mathbf{V}|_{fb} \cdot \mathbf{n} = \mathbf{q}_r \cdot \mathbf{n}$, equation (4.71) reduces to

$$(c'' - c|_{pm})(\mathbf{q}_r \cdot \mathbf{n} + \alpha^*) = -\phi \mathbf{D}_h \cdot \nabla c|_{pm} \cdot \mathbf{n}, \quad (4.72)$$

which now serves as the boundary condition.

In the absence of advection, or when $|\mathbf{q}_r \cdot \mathbf{n}| \ll \alpha^*$, equation (4.72) reduces to

$$\alpha^*(c'' - c|_{pm}) = -\phi \mathbf{D}^* \cdot \nabla c|_{pm} \cdot \mathbf{n}. \quad (4.73)$$

We note that if we accept (4.72), then $c''|_{fb} \neq c|_{pm}$ on the boundary, i.e., a jump in concentration takes place on the boundary. This is a consequence of introducing the transition zone and the 'well mixed zone' approximation.

When $|\mathbf{q}_r \cdot \mathbf{n}| \gg \alpha^*$, equation (4.72) reduces to

$$(c'' - c|_{pm})\mathbf{q}_r \cdot \mathbf{n} = -\phi \mathbf{D}_h \cdot \nabla c|_{pm} \cdot \mathbf{n}, \quad (4.74)$$

which is a boundary condition of the third kind, identical to (4.69), yet is based on different reasoning.

• **Phreatic surface.** We recall that the phreatic surface is defined as the surface at every point of which the water pressure is atmospheric. It serves as the upper boundary of the saturated domain. At the same time, it serves also as the lower boundary of the unsaturated one. Only the former case is considered here.

A detailed discussion on the phreatic surface and the conditions on it within the framework of a flow model, were presented in Subs. 2.3. Here we consider the condition on this boundary when modeling the transport of a chemical component in a fluid phase (= water). The boundary condition is derived from the requirement of *no-jump in the component's flux normal to the phreatic surface*.

We recall that the main difficulty associated with the phreatic surface as a boundary is that its shape and position are not known *a-priori*. However, since the pressure is atmospheric everywhere on this surface, or $h(\mathbf{x}, t) = z$, the equation that describes the shape of the phreatic surface may be written in the form $F = F(\mathbf{x}, t) = h(x, y, z, t) - z = 0$. This surface moves at a velocity \mathbf{u} ; equations (1.7), (1.8) and (1.9) are applicable, with $\nabla F = \nabla(h - z)$, and $\partial F/\partial t \equiv \partial h/\partial t$.

As is usually done in groundwater hydrology, we neglect the details of the movement of water through the unsaturated zone, and consider only some mean value of natural replenishment, \mathbf{N} , infiltrating at ground surface and reaching the phreatic surface as accretion, or natural replenishment. Let us denote the concentration of the considered component in the infiltrating water by c' , and assume (here and elsewhere in this section) that, in spite of concentration differences, the mass density of the water remains constant.

The component's total flux, relative to the moving phreatic surface, is given by $-c'(\mathbf{N} - \theta_{wr}\mathbf{u}) \cdot \mathbf{n}$, where θ_{wr} , assumed to be a constant, denotes the moisture content in the unsaturated zone, just above the phreatic surface.

The total flux in the saturated zone, relative to the moving phreatic surface, is expressed by $\phi [c(\mathbf{V} - \mathbf{u}) - \mathbf{D}_h \cdot \nabla c]$. Thus, the no-jump condition can be expressed as

$$\{\phi [c(\mathbf{V} - \mathbf{u}) - \mathbf{D}_h \cdot \nabla c]\} \cdot \mathbf{n} = c'(\mathbf{N} - \theta_{wr}\mathbf{u}) \cdot \mathbf{n}.$$

When combined with the flow boundary condition, (2.72), we obtain

$$(c - c') \left(\mathbf{N} \cdot \nabla F + \theta_{wr} \frac{\partial F}{\partial t} \right) - \phi (\mathbf{D}_h \cdot \nabla c) \Big|_{sat} \cdot \nabla F = 0. \quad (4.75)$$

We may insert $F = h(x, y, z, t) - z$ in the last equation.

This is a third type boundary condition for c . We note that $\llbracket c \rrbracket_{sat, unsat} \equiv c - c' \neq 0$. Thus, the unsaturated zone just above the phreatic surface acts as a 'well mixed zone' in the sense discussed earlier. However, we have simplified the expression for the flow through the transition zone by neglecting the dispersive-diffusive flux through it.

• **Seepage face.** The seepage face as a boundary was already discussed in Subs. 2.3. Water containing the considered component leaves the porous medium domain through the seepage face into the environment. Because no porous medium is present on the external side of this boundary, the condition of continuity of flux of a component, takes the form:

$$(\phi c \mathbf{V} - \phi \mathbf{D}_h \cdot \nabla c) \Big|_{pm} \cdot \mathbf{n} = (c \mathbf{V}) \Big|_{env} \cdot \mathbf{n}, \quad (4.76)$$

where symbols ' pm ' and ' env ' denote the porous medium domain and its environment, respectively, and we have assumed a stationary seepage face, $\mathbf{u} \equiv 0$. With:

$$c \Big|_{pm} = c \Big|_{env}, \quad (\phi \mathbf{V}) \Big|_{pm} \cdot \mathbf{n} = \mathbf{V} \Big|_{env} \cdot \mathbf{n},$$

the condition (4.76) reduces to the boundary condition

$$(\mathbf{D}_h \cdot \nabla c) \Big|_{pm} \cdot \mathbf{n} = 0. \quad (4.77)$$

This is a boundary condition of the second kind.

4.4. Macrodispersion

So far, the phenomenon of dispersion has been shown to be a consequence of the heterogeneity of the porous medium *at the microscopic level*, i.e., due to the presence of a solid matrix and a void space within the REV. A grain, a pore diameter, or the hydraulic radius of the pore space, may serve as a scale of heterogeneity for such a domain. This heterogeneity produces the velocity variations that take place at the microscopic level. The macroscopic level of description, obtained by averaging over an REV, and the dispersive flux,

were introduced as a means for circumventing the need to know the details of the velocity distribution and of other transport features at the microscopic level.

Contaminant transport phenomena take place within macroscopic domains (say, an aquifer) that may be conceptualized as either homogeneous or heterogeneous with respect to the relevant *macroscopic* geometrical parameters of the porous medium (e.g., porosity, permeability). In fact, *all subsurface domains encountered in practice are very heterogeneous*. For example, the permeability, usually, varies from point to point, even when the porous medium looks homogeneous. This heterogeneity is a dominant factor in subsurface transport. Because pressure propagates very fast, the effect of this inherent heterogeneity is less noticeable when considering fluid flow. However, its effect on the transport of chemical species is significant, because they are carried by relatively slow advective and diffusive fluxes.

It should be possible, at least in principle, to solve a transport problem at the macroscopic level in any heterogeneous domain in which the spatial variations of the permeability and other relevant coefficients are known. However, usually, we face a situation similar to that which is encountered at the microscopic level, viz., that the detailed information about the spatial variation of the relevant parameters is not available. The way to overcome the lack of information about the heterogeneity at the microscopic level (resulting from pore scale heterogeneity) is to use averaging over an REV. As a consequence, the phenomenon of dispersion was introduced. The same averaging, or smoothing, approach may also be applied to heterogeneities encountered at the macroscopic level. As a result, a new continuum is obtained for describing the porous medium and the phenomena that take place in it on a yet higher level, called the *megascopic level*.

As in the passage from the microscopic level to the macroscopic one, a new representative elementary volume is needed in order to perform the smoothing. We refer to such a volume as the *Representative Macroscopic Volume* (abbreviated as RMV) of the porous medium domain. If such a volume cannot be found, it is impossible to pass to the megascopic level. The characteristic size, ℓ^* , of this volume, is constrained by $d^* \ll \ell^* \ll L$, where d^* is a length characterizing the macroscopic heterogeneity that we wish to smooth out, and L is a length characterizing the considered porous medium domain. Obviously, the length scale of heterogeneity at the megascopic level will be much larger than that corresponding to the macroscopic one.

Similar to what happens during microscopic-to-macroscopic smoothing, here, the information about the heterogeneity at the macroscopic level appears at the megascopic one in the form of various coefficients. For this case, the coefficients reflect the effect of the spatial distribution of geometrical parameters (e.g., permeability and porosity) at the macroscopic level on the transport phenomena.

Let us derive the total flux of a γ -component at the megascopic level, by averaging (4.25) over an RMV. We obtain:

$$\begin{aligned}\overline{\theta \mathbf{J}^{t\gamma}} &= \overline{\bar{c}^f \mathbf{q}} + \overline{\theta (\mathbf{J}^\gamma + \mathbf{J}^{*\gamma})} \\ &= \overline{\bar{c}^f \mathbf{q}} + \overline{\hat{c}^f \hat{\mathbf{q}}} + \overline{\theta (\mathbf{J}^\gamma + \mathbf{J}^{*\gamma})} \approx \overline{\bar{c}^f \mathbf{q}} + \overline{\hat{c}^f \hat{\mathbf{q}}},\end{aligned}\quad (4.78)$$

where a bar over a macroscopic value indicates an average over an RMV (= megascopic value), with $\bar{c} = \theta \bar{c}^f$, and $(\hat{\cdot})$, defined by:

$$(\hat{\cdot}) = \overline{(\cdot)^f} - \overline{(\cdot)^f},$$

is the deviation of a macroscopic value of a quantity at any point within an RMV, from its average over the RMV. We note that the flux on the left-hand side of (4.78) (and hence all other terms) is per unit area of porous medium.

As could have been expected, the megascopic total flux contains two *new* additional dispersive fluxes which result from the variability of the relevant macroscopic quantities. One is $\overline{\hat{c}^f \hat{\mathbf{q}}}$, which will be referred to as the *macrodispersive flux* of the γ -component. The other is the average over the RMV of the sum of the dispersive and diffusive fluxes at the macroscopic level. Note that on the last part of (4.78), we have neglected the second dispersive flux as being much smaller than the first.

Altogether, the total flux is again the sum of an advective flux and a dispersive one. There is no analogy here to the diffusive flux, as we have neglected it. At very low velocities, we may not neglect the average of the macroscopic diffusive flux.

We have to express the dispersive flux at the megascopic level in terms of megascopic quantities, in the same manner as was done for describing transport at the macroscopic level. We usually *assume* that a Fickian-type dispersion law, e.g., (4.18), is also valid for the dispersion at the megascopic level. A *macrodispersivity*, A_{ijklm} , can be defined in the same way as was the dispersivity defined earlier in (4.19). Bear, [2], while developing the

vertically integrated mass balance equation for a component of a phase, suggested for the general case of an anisotropic porous medium, an expression for macrodispersivity which is analogous to the one used for dispersivity. For the isotropic case, a longitudinal and transversal macrodispersivities were suggested. Gelhar, [9] and Gelhar *et al.* [10], analyzed the dependence of macrodispersion on permeability variations. For horizontal flow in an isotropic confined aquifer they expressed the longitudinal macrodispersivity in the form:

$$A_L = \frac{1}{3} \frac{L_1^2 \sigma_{\ln k}^2}{a_T}, \quad (4.79)$$

in which L_1 is a correlation distance (= distance along which permeabilities are still correlated), and $\sigma_{\ln k}$ is the standard deviation of $\ln k$.

Altogether we may summarize this topic by suggesting that dispersion and macrodispersion are analogous phenomena, in that both are a consequence of velocity variations that are due to heterogeneity, but at different scales. Dispersion arises from velocity variations within the void space, caused by the presence of the solid surfaces. Macrodispersion is caused by variations in the permeability and porosity at the macroscopic level. In both cases, the total flux may be visualized as made up of an advective flux and a (hydrodynamic) dispersive one, written at the respective levels. The structure of the coefficient of dispersion is the same in both cases, and so is the relationship between the coefficient of dispersion, the dispersivity and the average velocity.

No need to add that once we have an expression for the macrodispersive flux, we insert it into the balance equation that is written for the domain regarded as a continuum at the megascopic level.

5. Modeling flow and solute transport with variable density

In the previous section, we have discussed the transport of a solute, or a contaminant, under the assumption that the concentration of the solute is sufficiently low, so as not to affect the viscosity and density of the fluid phase. However, under certain conditions, this assumption is not applicable, and we have to take into account the changes in viscosity and density produced by the changing concentration as flow takes place. As examples, we may mention the case of sea water intrusion into a coastal aquifer, the case of a contaminant like TCE, which is heavier than water, that may occur at concentrations that may strongly affect the water density and viscosity, and the case of flow in a salt dome, say in connection with investigations associated with radioactive repositories in geological formations.

As long as the fluid's density is not affected (or practically so), the flow and the transport problems can be *decoupled*. This means that, in principle, we can first solve the flow problem to determine the fluid's velocity, $\mathbf{V}(\mathbf{x}, t)$, everywhere within the considered domain. Then, this velocity can be used as a known input to the solute transport problem. In the case of *variable density flow*, the decoupling is not possible, as concentration changes affect the density, and the latter affects the velocity. The two problems have to be modeled and solved simultaneously for pressure and concentration of dissolved matter, as variables.

Let us briefly review the mathematical model of flow and contaminant transport under conditions of variable density. The conceptual model is essentially the same as the one presented above for three-dimensional flow, except that now we assume that the density and viscosity vary as a result of concentration variations. We continue to assume isothermal conditions.

In principle, changes in concentration affect the volume of the solution. Obviously, this phenomenon is more significant at high concentrations. For the sake of simplifying the analysis, we shall write the model in terms of

a normalized mass fraction of the total dissolved matter, abbreviated TDM (salts or organic compounds in aqueous solution), $C = C(\mathbf{x}, t)$, defined as:

$$C = \frac{\omega_{water} - \omega_{min}}{\omega_{max} - \omega_{min}}, \quad 0 \leq C \leq 1.0, \quad (5.1)$$

in which:

$$\omega_{water} = \frac{m_{TDM}}{m_{water}},$$

denotes the mass fraction of total dissolved matter in the aqueous solution, with m denoting mass, subscripts *min* and *max* indicating the minimum (could be zero) and maximum values of the total dissolved mass, respectively, in the aqueous solution, and:

$$\omega_{water} = \frac{c}{\rho}, \quad \omega_{min} = \frac{c_{min}}{\rho_{min}}, \quad \omega_{max} = \frac{c_{max}}{\rho_{max}}.$$

Although, in principle, the two variables of this problem are the pressure, p , and concentration, c , it is more convenient to solve the problem with a *reference piezometric head* and a mass fraction of dissolved matter as variables. The velocity is not a variable, as it can be expressed in terms of these two variables by an appropriate form of Darcy's law.

5.1. Constitutive relations

The exact dependence of density and viscosity on pressure and concentration has to be determined experimentally for each individual case. For example, one of the common constitutive relation used in many cases takes the form:

$$\rho = \rho(p, C) = \rho_o \exp \{ \beta_p(p - p_o) + \beta_c C \}, \quad \beta_p = \frac{1}{\rho} \frac{\partial \rho}{\partial p}, \quad \beta_c = \frac{1}{\rho} \frac{\partial \rho}{\partial C}, \quad (5.2)$$

in which ρ_o corresponds to $p = p_o$, and $C=0$, β_p denotes the coefficient of compressibility at constant mass fraction, and β_c is a coefficient that introduces the effect of changes in mass fraction of total dissolved matter on the fluid's density (at constant pressure).

Often, a linearized form of (5.2) is used:

$$\rho = \rho_o \{ 1 + \beta'_p(p - p_o) + \beta'_c C \}, \quad \beta'_p = \frac{1}{\rho_o} \frac{\partial \rho}{\partial p}, \quad \beta'_c = \frac{1}{\rho_o} \frac{\partial \rho}{\partial C}. \quad (5.3)$$

In what follows, we assume that for the considered range of pressures, we may employ the approximation $\beta'_c |\Delta C| \gg \beta'_p |\Delta p|$. Then, the constitutive relationship reduces to:

$$\rho = \rho_o (1 + \beta'_c C), \quad \beta'_c = \frac{1}{\rho_o} \frac{\partial \rho}{\partial C}. \quad (5.4)$$

Changes in concentration also affect fluid viscosity. A commonly used relationship is, [12, 11]:

$$\mu = \mu_o (1 + 1.85\omega - 4.1\omega^2 + 44.50\omega^3), \quad (5.5)$$

where μ_o is the viscosity at $\omega \equiv \omega_{water} = 0$. Note that $\beta'_p/\beta_p = \beta'_c/\beta_c = \rho/\rho_o$.

5.2. Motion equation

Darcy's law (2.4) remains valid also for variable density and viscosity. However, now the density and the viscosity depend on the (continuously variable) pressure and concentration (as we consider here only isothermal flow and transport). Using the approximate relationship (5.4), we introduce ρ_o as a reference density. We then define a *reference piezometric head*,

$$h^* = \frac{p}{g\rho_o} + z, \quad (5.6)$$

such that allows us to rewrite the motion equation in the form:

$$\mathbf{q}_r = -\mathbf{K}_o \cdot \frac{\mu_o}{\mu(C)} (\nabla h^* + \beta'_c C \nabla z), \quad \mathbf{K}_o = \frac{\mathbf{k}\rho_o g}{\mu_o}, \quad (5.7)$$

where \mathbf{k} and \mathbf{K}_o are the *permeability* and the *reference hydraulic conductivity*.

5.3. Mass balance equation for the fluid

The starting point is the three-dimensional mass balance equation (2.8). However, underlying this equation is the assumption that the advective flux of the total fluid mass is much smaller than the dispersive one. In the case of high density fluids, e.g., brine, we may encounter high density gradients, which produce large dispersive fluxes, if we express the dispersive flux of the fluid mass by $-\mathbf{D} \cdot \nabla \rho$, as the sum of (4.18) for all components. For sea

water intrusion, this effect may not be negligible. nevertheless, for the sake of simplicity, in what follows, we shall continue to make the above assumption. We can always introduce this effect when justified.

Since now, $\rho = \rho(p, C)$, the l.h.s. of (2.8) can be developed into:

$$\begin{aligned} \frac{\partial \rho \phi}{\partial t} &= \rho \frac{\partial \phi}{\partial t} + \phi \left(\frac{\partial \rho}{\partial p} \frac{\partial p}{\partial t} + \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t} \right) \\ &= \rho \{ (1 - \phi) \alpha + \phi \beta_p \} \frac{\partial p}{\partial t} + \phi \rho \beta_c \frac{\partial C}{\partial t}. \end{aligned} \tag{5.8}$$

Replacing the symbol $\rho \Gamma'$ by $\rho_R R_R - \rho Q_P$, in which R_R and Q_P denote the replenishment and pumping distributions, respectively, and following the steps that led to (2.19), the mass balance equation now takes the form:

$$\rho S_{op} \frac{\partial p}{\partial t} + \rho \phi \beta_c \frac{\partial C}{\partial t} = -\nabla \cdot \rho \mathbf{q}_r + \rho_R R_R - \rho Q_P, \tag{5.9}$$

in which S_{op} is defined by (2.55), and we note that on the r.h.s., we have the specific discharge relative to the solid, \mathbf{q}_r , expressed by (5.7).

The mass balance equation in terms of the reference piezometric head, h^* , takes the form:

$$\rho S_{oh^*} \frac{\partial h^*}{\partial t} + \rho \phi \beta'_c \frac{\partial C}{\partial t} = -\nabla \cdot \left[\rho \mathbf{K}_o \frac{\mu_o}{\mu(C)} (\nabla h^* + \beta'_c C \nabla z) \right] + \rho_R Q_R - \rho Q_P, \tag{5.10}$$

in which $S_{oh^*} = \rho_o g (\alpha + \phi \beta_p)$. This equation involves the two variables h^* and C , with $\rho = \rho(p, C)$.

5.4. Fluxes and mass balance of dissolved matter

We consider the following three fluxes of the total dissolved matter:

- The *advective flux* of the dissolved matter (per unit area of fluid) is $c\mathbf{V} \equiv \rho \omega_{max} C \mathbf{V}$, with \mathbf{V} obtained from (5.7), assuming $\mathbf{V}_s \ll \mathbf{V}$.
- The *diffusive flux* is expressed by Fick's law in the form of (4.13), with $\omega = C \omega_{max}$.
- The *dispersive flux*, in analogy to the diffusive flux, is assumed be expressed as $-\rho \mathbf{D} \nabla \omega$, with $\omega = C \omega_{max}$.

The mass balance equation for a variable density fluid (say, water) is essentially the same as (4.47), except that now the density varies with pressure and (primarily) with concentration. For the sake of simplicity, we shall assume that $R_d = 1$ (i.e., no adsorption), no chemical reactions, and no decay or growth phenomena occur. Using the relationship $c = \omega\rho$, and assuming $\omega_{min} = 0$, so that $C = \omega/\omega_{max}$, we can rewrite (4.47) for variable density in the form:

$$\frac{\partial\phi\rho C}{\partial t} = -\nabla\cdot\phi(\rho C\mathbf{V} - \rho\mathbf{D}\cdot\nabla C - \rho\mathcal{D}^*\cdot\nabla C) - \rho C Q_P + \rho_R C_R R_R, \quad (5.11)$$

in which the Q_P and R_R symbolically denote the spatial distributions of fluid (volumetric) rates of extraction and injection, respectively.

Equation (5.11) can also be written in the form:

$$\phi\rho\frac{DC}{Dt} = \nabla\cdot(\rho\mathbf{D}\cdot\nabla C + \rho\mathcal{D}^*\cdot\nabla C) + \rho_R R_R(C_R - C). \quad (5.12)$$

in which we have made use of the mass balance equation for the fluid, (2.8), with $\rho\Gamma = \rho_R R_R - \rho Q_P$. In (5.12), $DC/Dt \equiv \partial C/\partial t + \mathbf{V}\cdot\nabla C$ is the *material derivative* of C . This equation is usually referred to as the *Eulerian-Lagrangian formulation* of the mass balance equation for dissolved matter. This form is often used in numerical simulations.

Altogether, we have to solve two p.d.e.'s, (5.10) and (5.11) for the two variables h^* and C , noting that once we know C (and p from h^*), we can update ρ and μ , and use Darcy's law to determine the velocity, \mathbf{V} , required as input to the mass balance equation for the dissolved matter.

This is a *set of highly non-linear coupled equations*.

5.4.1. Initial and boundary conditions

Both equations require appropriate initial and boundary conditions. For the flow equation, these may be ones of prescribed reference head, h^* , prescribed normal flux, or a third type one, describing the flux through a (real or fictitious) semipervious boundary. For the mass balance of the dissolved matter, the conditions may also be the same as those presented for a constant density fluid: prescribed C , prescribed total normal flux, etc.

Let us exemplify some of these conditions by considering the case of sea water intrusion into a coastal aquifer, visualized as a problem of coupled flow

and solute transport, under conditions of variable density. A typical cross-section with sea water intrusion into a coastal aquifer is shown in Fig. 10. The flow domain is bounded by the impervious bottom, the sea bottom, the

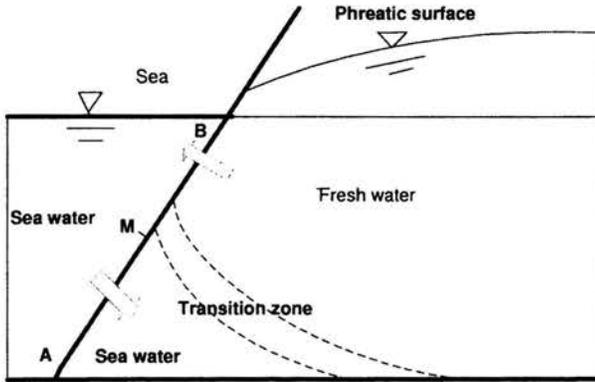


Figure 10: Sea water intrusion into a coastal aquifer.

seepage face, the phreatic surface and some arbitrary vertical surface on the right end side. We note the transition zone, across which the concentration varies between that of sea water and that of fresh water. It is possible that the zone of fresh water close to the sea may be very thin, or even not exist. It will continue to exist as long as fresh water is drained to the sea.

We'll focus on conditions for flow and transport on two boundary segments: the portion of the sea bottom (MB) through which water from the aquifer is drained into the sea, and the portion of the sea bottom (AM) through which sea water enters the aquifer. The two portions of the sea bottom are separated by a point M (or curve in a 3-d model) at which the fluid's velocity vanishes.

- **Outflow portion of the sea bottom.** For the flow model, the boundary condition along MB is one of specified pressure, which can easily be translated into a specified reference piezometric head. This pressure is dictated by the column of sea water above every point of the boundary.

For the transport mode, we assume that a well-mixed buffer zone exists on the sea bottom, that contains water that has just crossed the sea bottom boundary. Thus, it has the same concentration and density as on the land side of this boundary. Because the buffer zone is well mixed, there

is no diffusion nor dispersion there. The fluid's normal flux is, obviously, continuous. Accordingly, continuity of mass flux normal to the boundary requires that:

$$\phi(\rho C \mathbf{V} - \rho \mathbf{D} \cdot \nabla C - \rho \mathcal{D}^* \cdot \nabla C) \cdot \mathbf{n} = \phi \rho C \mathbf{V} \cdot \mathbf{n}, \quad (5.13)$$

or

$$\phi \rho (\mathbf{D} \cdot \nabla C + \mathcal{D}^* \cdot \nabla C) \cdot \mathbf{n} = 0. \quad (5.14)$$

This is the required boundary condition. We note an inconsistency due to the fact that the buffer zone is not taken into account when determining the pressure. This can easily be corrected; iterations will then be required.

• **Inflow portion of sea bottom.** Here also, the condition of continuity of the normal flux requires that

$$\phi(\rho C \mathbf{V} - \rho \mathbf{D} \cdot \nabla C - \rho \mathcal{D}^* \cdot \nabla C) \cdot \mathbf{n} = \phi \rho_{sea} C_{sea} \mathbf{V} \cdot \mathbf{n}, \quad (5.15)$$

or

$$\phi \rho (\mathbf{D} \cdot \nabla C + \mathcal{D}^* \cdot \nabla C) \cdot \mathbf{n} = \phi (\rho C - \rho_{sea} C_{sea}) \mathbf{V} \cdot \mathbf{n}. \quad (5.16)$$

This is the required boundary condition. Other conditions, like an impervious aquifer bottom, or a phreatic surface, are the same as for any solute transport problem, except that we have to modify them in view of the fact that the water density depends on the concentration.

More details on modeling sea water intrusion can be found in Bear, [4].

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