

# MODELING GROUNDWATER FLOW and CONTAMINANT TRANSPORT

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# Preface

Groundwater, extracted from deep geological formations (called aquifers) through pumping wells, constitutes an important component of many water resource systems. A spring constitutes an outlet for groundwater from an underlying aquifer to ground surface; its discharge rate may be strongly affected by pumping from the same aquifer in the vicinity of the spring. Water can be injected through specially designed wells into an aquifer, say, for storage purposes. A water table aquifer can also be artificially recharged through infiltration ponds. These are just a few examples of factor that may affect the management of a groundwater system. Decisions associated with such management include, for example,

- The volume that can be safely withdrawn annually from the aquifer.
- The location of pumping and artificial recharge wells, and their rates.
- The quality of the water to be maintained in the aquifer, and/or to be pumped from it.

In fact, in the management of water resources, the quantity and quality problems cannot be separated from each other. In many parts of the world, as a result of increased withdrawal of groundwater, often beyond permissible limits, the quality of groundwater has been continuously deteriorating, causing much concern to both suppliers and users. The quality deterioration may manifest itself in the form of an increase in the total salinity, or as increased concentrations of nitrates and other undesirable chemical species, or as increased concentrations of harmful pathogens.

Traditionally, hydrogeologist dealt with flow in aquifers, and with certain water quality aspects, e.g., salinization. Soil physicist and agronomists, in connection with agricultural activities, have modeled the movement of water and chemicals (e.g., fertilizers) in the unsaturated zone. The hydrogeologist, whose primary interest has been water in aquifers, regarded the unsaturated zone only as the domain through which water from precipitation passes on its way to replenish an underlying water table aquifer. The details of the actual movement of water through the unsaturated zone have been of little or no interest. The situation has completely changed with the rising interest in subsurface contamination. Clearly, interdisciplinary efforts, straddling nu-



merous areas of expertise, are now required to model and solve contamination problems of practical importance.

In recent years, in addition to the general groundwater quality aspects mentioned above, public attention has been focused on groundwater contamination by hazardous industrial wastes, on leachate from landfills and spills of oil and other toxic liquids, on agricultural activities, such as the use of fertilizers, pesticides, and herbicides, and on radioactive waste in repositories located in deep geological formations, to mention some of the more acute contamination sources. Although originating at ground surface, these contaminants (e.g., spilled oil, pesticides applied to an orchard, or leachate from a landfill), soon infiltrate through ground surface, percolate through the unsaturated zone, and find their way to groundwater in an underlying aquifer. Once reaching the aquifer, contaminants are transported with the moving groundwater, eventually reaching pumping wells, streams and lakes.

Sometimes, a toxic chemical may constitute a separate, nonaqueous, liquid phase, e.g., oil, that occupies part of the void space. Components of such toxic liquids may dissolve in percolating water, thus constituting a source for groundwater contamination. The volatile contaminant components may evaporate to become components of the gaseous phase (air) present in the void space. In the subsurface, while being transported with the water, the various contaminants undergo complex physical, chemical, and biological transformations. Chemical species carried by the water often interact with each other and with the soil, especially with the clay and organic fractions of the latter. Phenomena such as adsorption, ion exchange, chemical reactions, dissolution, volatilization, and biological decay, continuously affect the concentration of the chemical constituents present in the percolating water.

Data obtained by monitoring concentrations of hazardous contaminants in the subsurface, often call for remedial action. Regulations on quality standards may require cleanup of the contaminated aquifer and the unsaturated zone. The latter may be visualized as a huge physical-chemical-biological reactor in which many processes occur simultaneously among species present in the water, in nonaqueous fluids, and on the solid matrix. The biota present on the soil and in the fluids may also play an important role. Because of the way fluids behave in the unsaturated zone, cleaning that zone is often very complicated and costly, as it often requires sophisticated in situ chemical and biological methods.

Any plan of mitigation, cleanup operations, or control measures, once contamination has been detected in the subsurface, requires the prediction of pathways and fate of the contaminants, in response to certain planned remediation activities. Similarly, any monitoring or observation network must be based on the anticipated behavior of the system.

Management means making decisions to achieve goals, without violating specified constraints. Therefore, good management requires information on the response of the managed system to proposed activities. This information enables the planner, or the decision-maker, to compare alternative actions,

to select the best one, and to ensure that constraints are not violated. All such predictions can be obtained, within the framework of a considered management problem, by constructing and solving mathematical models of the investigated domain, and of the flow and solute transport phenomena that take place in it.

Using mathematical models for making prediction requires input data. The major role of the data is to enable model validation and calibration. The more accurate and complete are the collected field data, the more reliable are the values of model parameters obtained by model calibration, and, hence, also of the model's predictions. However, data gathering activities face the reality of uncertainty: subsurface geological formations are far too heterogeneous to provide the accurate detailed information required for their complete description. Nevertheless, since there is no other way but to use models in order to predict the future behavior of an investigated system, using whatever data that are available for model calibration cannot be avoided, in spite of the associated uncertainty. Various tools are available for coping with this uncertainty.

For most practical problems, because of the heterogeneity of the considered domain and the irregular shape of its boundaries, it is not possible to solve the mathematical models analytically. Instead, the mathematical model is transformed into a numerical one that can be solved by means of computer programs. Indeed, excellent computer programs are available for this purpose. Unfortunately, too often, practitioners use such available computer programs without really grasping the theory and assumptions underlying the models that they are solving. Our purpose in this book is to present not only the models that describe phenomena of flow and solute transport in aquifers, but also to emphasize the theoretical foundation and the various assumptions that simplify the complex reality to the extent that it can be described by rather simple and solvable models.

With this background, the major objectives of this book are:

*To construct conceptual and mathematical models that can provide the information required for making decisions associated with the management of groundwater resources, and the remediation of contaminated aquifers.*

More specifically,

- To describe the mechanisms that govern the movement of fluids and contaminants in aquifers and in the unsaturated zone.
- To construct well-posed mathematical models of saturated flow in three-dimensional porous medium domains and in aquifers, and of single and multiphase flow in the unsaturated zone.
- To construct well-posed mathematical models of transport of single and multiple chemical species in the unsaturated zone and in aquifers.

Three additional topics, strongly related to use of models for predicting flow and transport regimes in aquifers, within the framework of management, are discussed:

- The use of numerical models and computer codes as practical tools for solving the mathematical models.
- The issues of uncertainty associated with modeling.
- Certain mathematical tools for groundwater management.

With these objectives in mind, the book is aimed at practitioners, modelers, water resources managers, scientists, and researchers, who face the need to build and solve models of flow and contaminant transport in the subsurface. It is also suitable for graduate and upper level undergraduate students who are interested in such topics as groundwater, water resources, and environmental engineering. The basic scientific background needed is the concepts and terminologies of hydrology and hydraulics.

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## Chapter 7

# MODELING CONTAMINANT TRANSPORT

The issue of contamination of water in the subsurface was introduced in Subs. 1.1.5. In that subsection, we have also listed a number of the more common sources of subsurface contamination.

Our objective in this chapter is to develop complete mathematical models that describe the transport in the subsurface of contaminants dissolved in the water that occupies the void space, or part of it. These dissolved species determine groundwater quality. We use here the term ‘transport’ as an abbreviation for ‘movement, storage, and transformations’, with the term ‘transformations’ indicating changes in concentrations of dissolved chemical species as consequences of chemical reactions, and interphase transfers, such as dissolution of the solid matrix, and precipitation. Such transformations, which appear in the mass balance equation for a chemical species as source or sink terms, are also discussed in this chapter.

Accordingly, we shall start this chapter by discussing the flux of a chemical species, by different modes, then construct the mass balance equation for such species, and finally discuss the source/sink terms that describe chemical reactions and interphase transfers.

Although we are using here the term *contaminant*, to emphasize that our primary interest is groundwater contamination, the discussion, the modeling, etc. in this chapter is applicable to any chemical species dissolved in the water (e.g., a tracer) that travels through the void space of a porous medium domain.

As in previous chapters, we shall consider macroscopic level models that describe and facilitate the prediction of the transport of one or more (possibly interacting) chemical species in a single- or multi-phase system. Such predictions are required in order to plan the management of an aquifer, or the cleanup of the subsurface. In principle, such models are obtained by first understanding the relevant phenomena that occur at the microscopic level, i.e., at points *within* the fluid phase, and modeling these phenomena at that level. The macroscopic models are then derived by averaging the microscopic ones. Both modeling levels are discussed in Sec. 1.3.

In principle, the structure and content of a contaminant transport model is the same as that of a flow model. The main difference is that in the flow

model, the transported quantity is the mass of the fluid phase, while in a contaminant transport model, the transported quantity is the mass of the chemical species—the contaminant—carried by that phase. In the first case, the intensive quantity is the fluid mass density, while in the latter case, it is the concentration of the chemical species. Furthermore, we may have to consider, simultaneously, a number of interacting chemical species.

Note that although in this book we are interested primarily in groundwater in aquifers, especially with respect to groundwater quality and contaminant transport, we have also to consider the transport of contaminants through the unsaturated zone, as many chemical and biological activities that take place in this zone strongly affect the eventual contamination of groundwater in an underlying aquifer.

As explained in the previous chapter (see Sec. 6.5), in addition to water and air that together occupy the void space in the unsaturated zone (and water alone in the saturated zone), a third fluid phase—a Non-Aqueous Phase Liquid (NAPL)—may occupy part of the void space in both zones. In most cases, this NAPL (e.g., benzene and other hydrocarbons, and trichloroethylene) is also a contaminant. We have emphasized in the previous chapter that although a NAPL may be almost immiscible in water, its small, often very small, solubility is sufficient to render groundwater as being contaminated. In this chapter, we shall not treat the movement of NAPL as a separate, third phase, but focus only on contaminants that are dissolved in and carried by the water.

Figure 7.0.1 shows some typical cases of subsurface contamination:

- (a) The migration of a contaminant that is leached from a landfill; the leachate travels through the vadose and then through the (saturated) aquifer, eventually draining to a river.
- (b) An LNAPL (= Light NAPL) leaks from an underground storage tank and migrates through the vadose zone, eventually accumulating on an underlying water table.
- (c) Different routes through which a DNAPL (= Dense NAPL) and an LNAPL can contaminate an aquifer.

In all these cases, dissolved contaminants are transported in the subsurface. Our objective in this section is to discuss modes of transport of such contaminants and the laws that governs their fluxes. Unless stated otherwise, the discussion will be at the macroscopic level. As throughout this book, the presentation is limited to isothermal conditions, although (man-made or naturally occurring) temperature changes may significantly affect the transport of solutes.

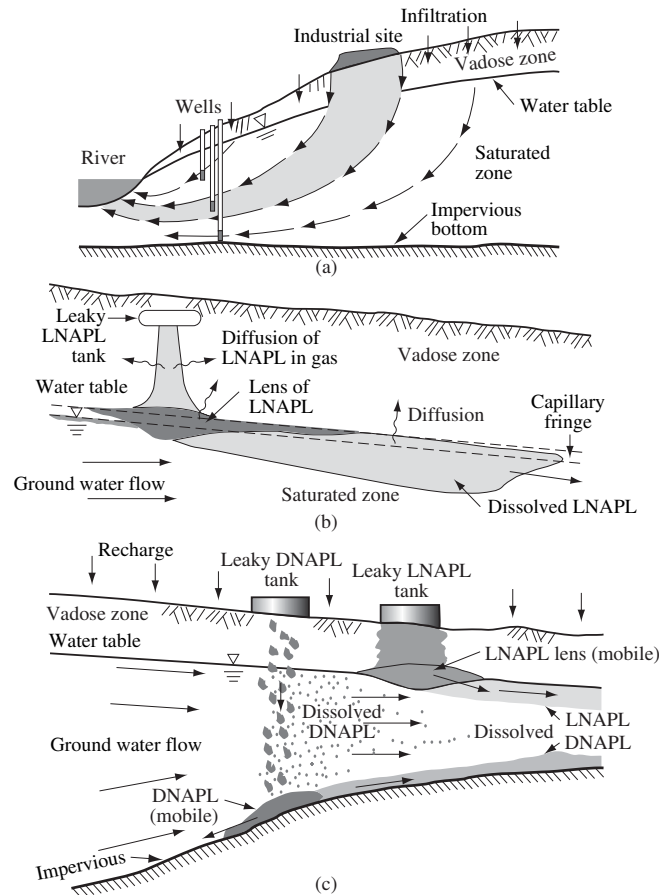


Figure 7.0.1: Examples of subsurface contamination.

## 7.1 Contaminant Fluxes

### 7.1.1 Measures of phase composition

Liquid and gas phases are comprised of many chemical species. This statement is also valid for the solid matrix. However, our main interest is in the aqueous phase that occupies the entire void space in the subsurface, or part of it. This phase is comprised primarily of water ( $\text{H}_2\text{O}$ ), with minute quantities of various chemical species dissolved in it. Although chemical reactions that involve solid matrix minerals, e.g., dissolution and precipitation, may play a significant role in changing the structure and configuration of the solid matrix, unless otherwise specified, we shall simplify the discussion by assuming that the numerous minerals constituting the soil's solid matrix are

represented by a single pseudo-species, referred to as ‘solid’. On the other hand, each fluid phase that occupies the void space, or part of it, whether a liquid or a gas, may be composed of more than a single species of interest. It is, therefore, necessary to consider the composition of each individual phase. The quantity of a given chemical species within a phase may be expressed in a number of ways.

**Concentration.** The concentration of a component indicates the quantity of the latter in a unit volume of fluid phase. It can, thus, be measured in different ways, depending on the selected units for quantity and volume. As everywhere in this book, we shall use a subscript to denote a *phase* (e.g.,  $\alpha$ ), and a superscript to denote a *component* (e.g.,  $\gamma$ ). To emphasize that we measure the concentration at a point in a porous medium domain, or in a sample taken at such point, we shall assume that the fluid’s volume is  $\mathcal{U}_{o\alpha}$ , i.e., the volume of the  $\alpha$ -phase within an REV.

Sometimes, the chemical species is referred to as a ‘solvent’ if it is the predominant species in a phase, or as a ‘solute’ if it constitutes only a small portion of a phase.

The common units for expressing the quantity of a species are the *gram*, abbreviated g (expressing the mass of the component), the *mole* (expressing the number of basic entities, such as molecules or ions), and the *equivalent* (expressing the number of equivalent weights). One mole of a substance contains as many atoms (or molecules, etc.) as there are atoms in exactly 12 g of carbon ( $^{12}\text{C}$ ). This number is approximately  $6.0221415 \times 10^{23}$ , also known as the *Avogadro’s number*.

In the SI system of units, the *kilogram* (= 1000 grams) is the standard unit for mass. The standard unit for volume in the metric system is the *liter*, defined as the volume of one kilogram of water at 20°C and pressure of one atmosphere. Other units of volume are the milliliter ( $\text{m}\ell = 1/1000$  of a liter), equal to the cubic centimeter ( $\text{cc}, \text{cm}^3$ ).

**Mass concentration.** The mass concentration,  $c_\alpha^\gamma$  ( $\equiv \rho_\alpha^\gamma$ ), expresses the mass of a  $\gamma$ -species, per unit volume of a fluid  $\alpha$ -phase:

$$c_\alpha^\gamma = \frac{m_\alpha^\gamma}{\mathcal{U}_{o\alpha}}, \quad (7.1.1)$$

where  $m_\alpha^\gamma$  denotes the mass of  $\gamma$  within an REV. This is the most commonly used measure for describing water quality. The common units are  $\text{g}/\ell$  (= grams of  $\gamma$  per liter of fluid), or  $\text{mg}/\ell$  (= milligrams of  $\gamma$  per liter of fluid).

**Molar concentration.** The molar concentration, or **molarity**,  $[c^\gamma]$ , expresses the number of  $\gamma$ -moles,  $N_\alpha^\gamma$ , per unit volume of the  $\alpha$ -phase:

$$[c_\alpha^\gamma] = \frac{N_\alpha^\gamma}{\mathcal{U}_{o\alpha}} = \frac{c_\alpha^\gamma}{M^\gamma}, \quad (7.1.2)$$

where  $M^\gamma$  is the molecular mass of the  $\gamma$ -species. In thermodynamic relationships, moles are the only measure of concentration. The common units are moles of  $\gamma$  per liter of  $\alpha$ -phase (mol/ $\ell$ ), or mol/m<sup>3</sup> ( $\equiv$  mmol/ $\ell$ ).

**Molar fraction.** The molar fraction, or mole fraction,  $n_\alpha^\gamma$ , is useful when dealing with modeling transport of contaminants with chemical reactions (*= reactive transport*). It is defined as the ratio between the number of moles of  $\gamma$  and the total number of moles in the  $\alpha$ -phase:

$$n_\alpha^\gamma = \frac{N_\alpha^\gamma}{N_\alpha}, \quad N_\alpha = \sum_{(\gamma)} N_\alpha^\gamma, \quad \sum_{(\gamma)} n_\alpha^\gamma = 1. \quad (7.1.3)$$

**Equivalent concentration,**  $c_\alpha^{\gamma eq}$ , is another useful measure, defined as

$$c_\alpha^{\gamma eq} = \frac{N_\alpha^{\gamma eq}}{\mathcal{U}_{o\alpha}}, \quad (7.1.4)$$

where  $N_\alpha^{\gamma eq}$  denotes the number of *equivalents* of  $\gamma$  in  $\alpha$ . It gives the quantity of  $\gamma$  that reacts with, or equal to the combining value of, a specified quantity of another substance with respect to a given reaction. For *redox* reactions (see any text on chemistry or geochemistry, e.g., Appelo and Postma (2005)), the mass of a substance associated with the loss or gain of one mole of electrons is commonly referred to as the ‘equivalent weight’ of that substance with respect to the reaction. In this case,  $c_\alpha^{\gamma eq} = c_\alpha^\gamma i^\gamma / M_\alpha$ , with  $i^\gamma$  denoting the *ionic charge* or *valence* of  $\gamma$ .

Other often encountered definitions of concentration are the *equivalents per liter* ( $\equiv$  eq/ $\ell$ ), defined as the number of moles of a solute, multiplied by the *valence* of the solute species, per liter of solution, and *equivalents per million*, epm, defined as the number of moles of a solute, multiplied by the *valence* of the solute species, per 10<sup>6</sup> g of solution.

**Mass fraction.** The mass fraction,  $\omega_\alpha^\gamma$ , is the mass of a  $\gamma$ -species per unit mass of the  $\alpha$ -phase:

$$\omega_\alpha^\gamma = \frac{m_\alpha^\gamma}{m_\alpha} = \frac{c_\alpha^\gamma}{c_\alpha}, \quad \sum_{(\gamma)} \omega_\alpha^\gamma = 1. \quad (7.1.5)$$

This measure is applicable to a  $\gamma$ -species in solution in a fluid-phase, or as part of a solid phase. The unit ppm, ‘parts per million’, defines the number of grams of solute per million grams of solution. The mass fraction is widely used for aqueous contaminants in the saturated zone.

**Electrical conductivity,** EC, measures the ability of a solution to conduct electrical current. Although this is not a measure of concentration, it is included here because it is related to the ions that are present in the solution. The unit is the reciprocal of ohm-meters, or, in the SI system, siemens per meter (S/m). Often, the EC is measured in the reciprocal of milliohms or, microohms, known as millimhos ( $\equiv$  mS), or micromhos ( $\equiv$   $\mu$ S), respectively.



### 7.1.2 Advective flux

We consider the transport of a  $\gamma$ -contaminant, actually, any dissolved chemical species, within a fluid phase that occupies the entire void space, or part of it, at a volumetric fraction  $\theta$ . With  $\mathbf{V}$  denoting the (intrinsic phase) average (mass-weighted) velocity of the phase, and  $c^\gamma$  denoting the (intrinsic phase) average concentration of the contaminant (expressed as mass of contaminant per unit phase volume), the *advective flux*,  $\mathbf{J}_{\text{adv}}^\gamma$ , of the considered component (= contaminant) is given by the product

$$\mathbf{J}_{\text{adv}}^\gamma = \theta \mathbf{V} c^\gamma. \quad (7.1.6)$$

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

### 7.1.3 Diffusive flux

#### A. Definition of diffusive flux and Fick's law

A fluid phase is, usually, composed of a number of *chemical species* (Subs. 1.3.1), each made up of a large number of identical molecules (ions, atoms, etc.) that are in constant random motion (Brownian motion). Note that a solvent is one of the chemical species. At the microscopic level, each intensive quantity of a chemical species of a phase, e.g., concentration, may be regarded as a continuum. The behavior of this continuum is obtained by averaging the behavior of the individual molecules that comprise it. For example, each molecule has mass, momentum, and energy. The transport of these extensive quantities at the microscopic level is obtained by averaging their transport by the individual molecules. Let superscript  $\gamma$  denote a dissolved chemical species. We shall start by considering what happens at the microscopic level, without using any symbol to denote this fact.

The *total flux*,  $\mathbf{j}^{tE}$ , of an extensive quantity  $E$ , and  $\mathbf{j}^{tE^\gamma}$  of the extensive quantity  $E^\gamma$ , of a  $\gamma$ -species, can be expressed as

$$\mathbf{j}^{tE} = e \mathbf{V}^E, \quad \mathbf{j}^{tE^\gamma} = e^\gamma \mathbf{V}^{E^\gamma}, \quad (7.1.7)$$

with

$$\mathbf{j}^{tE} = \sum_{(\gamma)} \mathbf{j}^{tE^\gamma} = \sum_{(\gamma)} e^\gamma \mathbf{V}^{E^\gamma}, \quad (7.1.8)$$

where  $e$  (= quantity of  $E$  per unit volume of the phase) 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 and  $\mathbf{V}^{E^\gamma}$  of a particle of an  $E^\gamma$ -continuum of a  $\gamma$ -species, both of a phase, are defined as:

$$\mathbf{V}^E \equiv \left. \frac{\partial \mathbf{x}^E}{\partial t} \right|_{\xi^E = \text{const.}}, \quad \mathbf{V}^{E^\gamma} \equiv \left. \frac{\partial \mathbf{x}^{E^\gamma}}{\partial t} \right|_{\xi^{E^\gamma} = \text{const.}}, \quad (7.1.9)$$

where  $\mathbf{x}^E$  denotes the position vector of an  $E$ -particle with material coordinates  $\boldsymbol{\xi}^E$ . We recall that  $\mathbf{V}(\equiv \mathbf{V}^m)$  denotes the mass weighted velocity, i.e., the velocity of the extensive quantity mass (i.e.,  $E \equiv m$ ).

Physically,  $e\mathbf{V}^E$  represents the quantity of  $E$  passing through a unit area of the  $E$ -continuum, normal to the direction of  $\mathbf{V}^E$ , per unit time. This flux may be expressed as the sum of two fluxes:

$$e\mathbf{V}^E = e\mathbf{V} + e(\mathbf{V}^E - \mathbf{V}) \equiv e\mathbf{V} + \mathbf{j}^E. \quad (7.1.10)$$

We have, thus, decomposed the total flux of  $E$ ,  $\mathbf{j}^{tE}$ , into two parts:

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

$$\mathbf{j}^E = e(\mathbf{V}^E - \mathbf{V}). \quad (7.1.11)$$

We may now apply the above definitions to the particular case in which  $E^\gamma$  is the mass of a  $\gamma$ -species of a fluid phase, with  $e^\gamma \equiv \rho^\gamma \equiv c^\gamma$ , and with  $c^\gamma$  referred to as the *concentration* of the  $\gamma$ -species. For this case, the total mass flux is expressed by  $c^\gamma\mathbf{V}^\gamma$ . When decomposed into two parts, we obtain:

$$c^\gamma\mathbf{V}^\gamma = c^\gamma\mathbf{V} + c^\gamma(\mathbf{V}^\gamma - \mathbf{V}) = c^\gamma\mathbf{V} + \mathbf{j}^\gamma, \quad (7.1.12)$$

where

$$\sum_{\gamma=1}^N c^\gamma\mathbf{V}^\gamma \equiv \rho\mathbf{V}, \quad \text{and} \quad \mathbf{j}^\gamma = c^\gamma(\mathbf{V}^\gamma - \mathbf{V}), \quad (7.1.13)$$

is the *diffusive mass flux* of the  $\gamma$ -species, usually referred to as *molecular diffusion*. We note that for all ( $N$ ) species within a phase,

$$\sum_{\gamma=1}^N \mathbf{j}^\gamma = \sum_{\gamma=1}^N c^\gamma(\mathbf{V}^\gamma - \mathbf{V}) = \sum_{\gamma=1}^N \rho(\mathbf{V}^\gamma - \mathbf{V}) = 0. \quad (7.1.14)$$

We have thus decomposed the total mass flux of a  $\gamma$ -species into two parts:

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

Both fluxes are in terms of mass of chemical species per unit area of *fluid phase*.

Equations (7.1.12) and (7.1.13) give the total and the diffusive mass fluxes of a considered chemical species, respectively.

Still at the microscopic level, we consider a fluid containing only two species:  $\gamma$  and  $\delta$  (= *binary system*). The mass flux of molecular diffusion of

the  $\gamma$ -species,  $\mathbf{j}^\gamma$ , 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, in the form:

$$\mathbf{j}^\gamma = c^\gamma(\mathbf{V}^\gamma - \mathbf{V}) = -\rho\mathcal{D}^{\gamma\delta}\nabla\omega^\gamma, \quad \sum_{(\gamma)} \mathbf{j}^\gamma = 0, \quad (7.1.15)$$

$\omega^\gamma = \rho^\gamma/\rho$  denotes the mass fraction of  $\gamma$ , and the scalar  $\mathcal{D}^{\gamma\delta}$  is the *coefficient of molecular diffusion* (dims.  $\text{L}^2/\text{T}$ ) of the  $\gamma$ -component in a fluid phase that contains only two components,  $\gamma$  and  $\delta$ .

The diffusive flux of the other component,  $\delta$ , is given by  $\mathbf{j}^\delta = -\rho\mathcal{D}^{\delta\gamma}\nabla\omega^\delta$ . Note that the condition  $\mathbf{j}^\gamma + \mathbf{j}^\delta = 0$  implies that for a binary system  $\mathcal{D}^{\gamma\delta} = \mathcal{D}^{\delta\gamma}$ . It is assumed that  $\mathcal{D}^{\gamma\delta}$  is independent of  $c^\gamma$ . However, it is, in general, a function of pressure and temperature.

When  $\nabla\rho = 0$ , i.e., a *homogeneous fluid*, we may write Fick's law, (7.1.15), in terms of the concentration,  $c^\gamma$ , as

$$\mathbf{j}^\gamma \equiv c^\gamma(\mathbf{V}^\gamma - \mathbf{V}) = -\mathcal{D}^{\gamma\delta}\nabla c^\gamma. \quad (7.1.16)$$

Fick's law can also be written in terms of the gradient of molar concentration,  $[c^\gamma]$ .

Typical values of  $\mathcal{D}^{\gamma\delta}$  at 25°C, for a solute in an aqueous phase, are in the range of  $5\text{--}100 \times 10^{-6} \text{ cm}^2/\text{s}$ . For example, for  $\text{Ca}^{2+}$ ,  $\mathcal{D}^{\gamma\delta} = 7.9 \times 10^{-6} \text{ cm}^2/\text{s}$ ; for  $\text{K}^+$ ,  $\mathcal{D}^{\gamma\delta} = 19.6 \times 10^{-6} \text{ cm}^2/\text{s}$ ; and for  $\text{Cl}^-$ ,  $\mathcal{D}^{\gamma\delta} = 20.3 \times 10^{-6} \text{ cm}^2/\text{s}$ . Typical values for a dilute component in an air are: for water vapor,  $\mathcal{D}^{\gamma\delta} = 2.2 \times 10^{-1} \text{ cm}^2/\text{s}$ ; and for TCE vapor,  $\mathcal{D}^{\gamma\delta} = 7.8 \times 10^{-2} \text{ cm}^2/\text{s}$ . The diffusivity of a broad range of compounds as a function of temperature and pressure are given by Poling *et al.* (2000). Fick's law, (7.1.15), also holds, as an approximation, for the diffusive flux of a  $\gamma$ -component in a multicomponent system, as long as the  $\delta$ -component is the solvent component and all components, except  $\delta$  and  $\gamma$ , are at dilute concentrations. Another case where Fick's law holds is when all components are at dilute concentrations, except for the  $\delta$ -component. Then,  $\mathbf{j}^\lambda = -\rho\mathcal{D}^{\lambda\delta}\nabla\omega^\lambda$  for  $\lambda \neq \delta$ , and

$$\mathbf{j}^\delta = -\sum_{\gamma(\neq\delta)} \mathbf{j}^\gamma = \sum_{\gamma(\neq\delta)} \rho\mathcal{D}^{\gamma\delta}\nabla\omega^\gamma. \quad (7.1.17)$$

This last equation follows from the necessary condition:  $\sum_{(\gamma)} \mathbf{j}^\gamma = 0$ .

## B. Diffusion of ions and electroneutrality

The diffusion of an ion (considered as a  $\gamma$ -species) in an aqueous solution, away from any charged solid surface, is affected by the electrical field generated by all ions in the solution. In a dilute solution, this diffusive mass flux is given by

$$\mathbf{j}^\gamma = -\frac{\rho\mathcal{F}}{RT}z^\gamma\mathcal{D}^{\gamma\gamma}\omega^\gamma\nabla\varphi_e - \rho\mathcal{D}^{\gamma\delta}\nabla\omega^\gamma, \quad (7.1.18)$$

where  $\varphi_e$  denotes the potential of the electrical field, and  $z^\gamma$  is the electrical charge of the ion. Here,  $\mathcal{F}$  is *Faraday's constant*, defined as the charge of one mole of singly-charged ions ( $= 9.65 \times 10^4$  Coulombs/mole). Equation (7.1.18) is derived from the *Nernst-Planck equations* (Probstein, 1994).

It is observed experimentally that in (non-organic) electrolytic solutions, the condition of *electroneutrality* holds: the net charge at any given point in a solution, away from charged surfaces, is essentially zero. That is,

$$\sum_{(\lambda)} z^\lambda n^\lambda = 0. \quad (7.1.19)$$

Electroneutrality requires that the diffusion fluxes satisfy the condition

$$\sum_{(\lambda)} z^\lambda \mathbf{j}^\lambda / M^\lambda = 0. \quad (7.1.20)$$

The electrical field between the ions, which is proportional to the gradient,  $-\nabla\varphi_e$ , counteracts the tendency of molecular diffusion to disturb charge neutrality. Therefore, by substituting (7.1.18) into the condition (7.1.20) and solving for  $-\nabla\varphi_e$ , we obtain

$$-\nabla\varphi_e = \frac{RT}{\mathcal{F}} \frac{\sum_{(\lambda)} z^\lambda \mathcal{D}^\lambda \nabla\omega^\lambda / M^\lambda}{\sum_{(\lambda)} (z^\lambda)^2 \mathcal{D}^\lambda \omega^\lambda / M^\lambda}. \quad (7.1.21)$$

Substituting this expression into (7.1.18) gives

$$\mathbf{j}^\gamma = z^\gamma \rho \mathcal{D}^\gamma \omega^\gamma \frac{\sum_{(\lambda)} z^\lambda \mathcal{D}^\lambda \nabla\omega^\lambda / M^\lambda}{\sum_{(\lambda)} (z^\lambda)^2 \mathcal{D}^\lambda \omega^\lambda / M^\lambda} - \rho \mathcal{D}^\gamma \nabla\omega^\gamma. \quad (7.1.22)$$

This expression is the diffusive mass flux of an ionic species in an electrically neutral dilute solution; it is used for modeling the transport of multiple ionic species (Lichtner, 1995).

### C. Macroscopic Fick's law

Our next step is to average the microscopic level advective and diffusive flux expressions presented above in order to obtain their macroscopic counterparts. This goal can be achieved by volume averaging over an REV (Sec. 1.3.3), or by various methods of 'homogenization' (Subs. 1.3.4).

In the passage from (7.1.16) to its macroscopic counterpart, the configuration of the solid-fluid interface, and conditions on it, affect the transformation of the (local) concentration gradient into a gradient of the average concentration (which is the state variable at the macroscopic level). Bear and Bachmat (1990), who used volume (REV) averaging, presented 'averaging rules', which should be employed in order to average mathematical models written at the microscopic level. We recall that taking an average involves integration (e.g.,

(1.3.2)), which takes into account the configuration and the conditions on the domain over which integration is performed. Following Bear and Bachmat (1990), and noting the various underlying assumptions, we average (7.1.15) for a fluid of constant density and constant coefficient of molecular diffusion, obtaining an expression for the macroscopic form of Fick's law of molecular diffusion. It expresses the macroscopic diffusive flux,  $\mathbf{J}^\gamma$ , of a  $\gamma$ -species within a fluid phase that occupies the entire void space, or part of it, in the form:

$$\mathbf{J}^\gamma = -\mathcal{D}^\gamma \mathbf{T}^*(\theta) \cdot \nabla c^\gamma = -\mathcal{D}^{*\gamma}(\theta) \cdot \nabla c^\gamma, \quad (7.1.23)$$

where  $c^\gamma (\equiv \overline{c^\gamma}^\alpha)$  is now the concentration of the  $\gamma$ -species at the macroscopic level,  $\theta$  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*. Note that  $\mathbf{J}^\gamma$  denotes the flux of  $\gamma$  *per unit area of the fluid within a porous medium cross-section*. For brevity, we have dropped the superscript  $\delta$  in  $\mathcal{D}^{\gamma\delta}$ . For saturated flow, we replace  $\theta$  by the porosity,  $\phi$ .

The symbol  $\mathbf{T}^*$ , a second rank symmetric tensor, represents the *tortuosity* of the porous medium (e.g., Bear and Bachmat, 1990). In an isotropic porous medium, the components of the tortuosity tensor,  $\mathbf{T}_{ij}^*$ , may be represented as  $\mathbf{T}^* \delta_{ij}$ , in which  $\mathbf{T}^* (< 1)$  is a scalar tortuosity, and  $\delta_{ij}$  is the Kronecker delta, with  $\delta_{ij} = 1$  for  $i = j$ , and  $\delta_{ij} = 0$  for  $i \neq j$ .

In indicial notation, (7.1.23) takes the form:

$$J_i^\gamma = -\mathcal{D}^\gamma \mathbf{T}_{ij}^*(\theta) \frac{\partial c^\gamma}{\partial x_j}, = -\mathcal{D}_{ij}^{*\gamma}(\theta) \frac{\partial c^\gamma}{\partial x_j}. \quad (7.1.24)$$

Note that *Einstein summation convention*, introduced in Subs. 4.1.4, is used in (4.1.4), as in all indicial notation equations in this book.

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

$$\mathbf{J}^\gamma = -\rho \mathcal{D}^{*\gamma}(\theta) \cdot \nabla \omega^\gamma, \quad (7.1.25)$$

where all variables and the coefficient are at the macroscopic level. Solute diffusion is also affected by the fact that the fluid's viscosity near the solid surfaces is higher than that in the interior of the fluid phase (Olsen and Kemper, 1968). We could include this affect as a factor affecting  $\mathcal{D}^{*\gamma}$ .

The tortuosity of a phase is a macroscopic geometrical coefficient that expresses the effects of the microscopic surface that bounds that phase on the diffusive flux. In fact, Bear and Bachmat (1990) show that the same tortuosity appears when considering the diffusive flux of any extensive quantity, say heat, that is confined to the fluid-occupied domain. As such, it depends on the configuration of the phase within the void space. Hence, in systems with multiple phases, each of the tortuosity components is a function of the saturations. Some authors relate the tortuosity in an isotropic porous medium to the volumetric fraction of the phase. For example, Millington (1959) gave

the equation

$$T^*(\theta) = \frac{\theta^{7/3}}{\phi^2}. \quad (7.1.26)$$

Note that when used to express the flux *per unit area of porous medium*, the tortuosity given by (7.1.26) takes the form  $\theta T^*(\theta) = \theta^{10/3}/\phi^2$ . Because the value of the tortuosity falls in the range zero to one, the value of the diffusivity in a fluid that occupies the entire void space, or part of it, is smaller than the corresponding value in an open fluid body.

#### D. Surface diffusion

Surface diffusion is the phenomenon of the net motion on the solid's surface of adsorbed atoms (often referred to as 'adatoms'), or molecules, ions or clusters of adatoms. When integrated over the entire surface area within a unit volume of porous medium, it is expressed as a macroscopic flux analogous to the diffusive flux that results from the random motion of the ions or atoms of a chemical species within the fluid that occupies the void space, or part of it. In fact, surface diffusion will also occur within the films that coat the solid surface in voids occupied by air in the unsaturated zone. Surface diffusion could be significant in fine grained porous media, e.g., clay, due to their huge specific surface.

An important example is the compacted clay or *bentonite* that serves as a barrier to radionuclides in a geological repository of high-level nuclear waste. Due to its huge specific surface, the barrier effect is achieved by adsorbing the escaped radionuclides; nevertheless, surface diffusion may play an important role since very long time periods are considered. Jahnke and Radke (1987) visualized the total (macroscopic) flux of a  $\gamma$ -ion as composed of two parts:  $J_{\text{diff}}^\gamma$ , which is the usual Fickian diffusion, and  $J_{\text{s.diff}}^\gamma$ , which describes surface diffusion, with

$$J_{\text{diff.total}}^\gamma = J_{\text{diff}}^\gamma + J_{\text{s.diff}}^\gamma, \quad (7.1.27)$$

in which both fluxes are described as Fickian expressions, i.e., both fluxes are proportional to the gradients in the respective concentrations. The model will then involve two variables: concentration in the fluid, and concentration adsorbed on the solid. Jahnke and Radke (1987) developed an expression for an equivalent diffusive flux that combines the two phenomena under the assumption of an equilibrium ion-exchange isotherm.

The subject of surface diffusion will not be further considered in this book.

#### 7.1.4 Hydrodynamic dispersion

We shall start by considering the transport of a contaminant (actually, any solute) in a single fluid phase that occupies the entire void space. Later, we shall extend the discussion to multiple phases.

Consider the flow of a fluid phase ( $f$ ), say, water, through a porous medium domain. At some initial time, let a portion of this fluid phase be labeled by

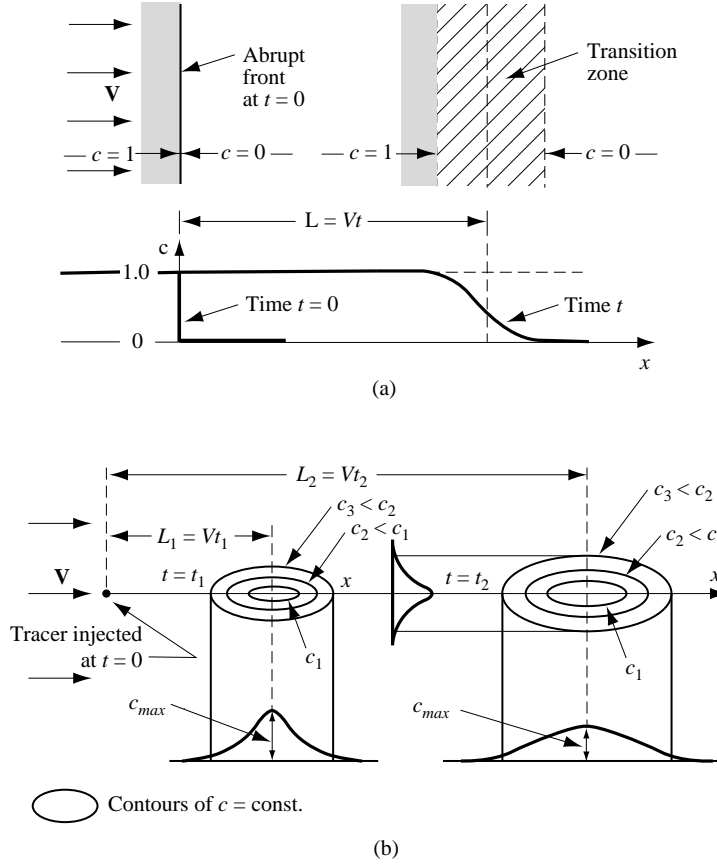


Figure 7.1.1: Longitudinal and transversal spreading of a solute. (a) Longitudinal spreading of an initially sharp front, (b) Spreading of a solute slug injected at a point.

some identifiable solute, a tracer. Let us start by conducting two *conceptual* field experiments.

Figure 7.1.1a shows saturated, (macroscopic) two-dimensional uniform flow, at an average velocity  $\mathbf{V} (\equiv \overline{\mathbf{V}}^f)$ , in the  $x$ -direction, in a porous medium domain, say, an aquifer. At an initial time,  $t = 0$ , an (assumed) abrupt straight line front divides the domain into two parts: one,  $x < 0$ , occupied by water with a dissolved solute at the concentration  $c = 1$ , and the other,  $x \geq 0$ , occupied by water at the solute concentration of  $c = 0$ . Using Darcy's law to calculate  $\mathbf{V} (= -(\mathbf{K}/\phi) \cdot \nabla h)$ , we may obtain the position of the (assumed) abrupt front, at  $x = L$ , at any later time,  $t$ , through the expression  $L = \mathbf{V}t$ . *On the basis of Darcy's law alone*, the two kinds of fluids would continue to occupy distinct subdomains, separated by an abrupt moving front.

However, in our ‘experiment’, by measuring concentrations at a number of observation wells scattered in the domain, we observe that no such front exists. Instead, we observe the development of a *transition zone* across which the solute concentration varies from  $c = 1$  to  $c = 0$ . Experience shows that as flow continues, the width of the transition zone increases. This spreading of the solute-labeled fluid, and the evolution of a transition zone, instead of a sharp front, cannot be explained by the average movement of the fluid at a velocity calculated by Darcy’s law.

As a second (conceptual) experiment, consider the injection of a small quantity of tracer at a point  $x = 0, y = 0$ , at some initial time,  $t = 0$ , into a tracer-free (macroscopic) two-dimensional uniform flow in a porous medium domain. Making use of the (averaged) velocity as calculated by Darcy’s law, we should expect the tracer-labeled fluid slug to move as a volume of fixed shape, reaching the point  $x = \mathbf{V}t$  at time  $t$ . Again, field observations (shown in Fig. 7.1.1b) reveal a completely different picture. We observe a spreading of the solute, not only in the direction of the (averaged) uniform flow, but also *normal to it*. The area occupied by the solute-labeled fluid, which has the shape of an ellipse in the two-dimensional flow domain considered here, will continue to grow, both *longitudinally*, i.e., in the direction of the uniform flow, and *transversely*, i.e., normal to it. The concentration peak appears to move at the averaged velocity. Curves of equal concentration have the shape of confocal ellipses. Again, this spreading cannot be explained by considering the averaged flow alone, especially noting the spreading perpendicular to the direction of the uniform averaged flow, and the ever-growing subdomain occupied by solute-labeled fluid.

The spreading phenomenon in a porous medium domain as described above is called *hydrodynamic dispersion*. It is an unsteady, *irreversible process* (in the sense that the initial tracer distribution cannot be obtained by reversing the direction of the uniform flow) in which the mass of a tracer continuously ‘mixes’ with the non-labeled portion of the moving fluid.

The phenomenon of dispersion may be demonstrated also by a simple laboratory experiment. Consider steady flow of water at a constant discharge,  $Q$ , in a column of homogeneous porous material. At  $t = 0$ , tracer-marked water (e.g., water with NaCl at a concentration that is sufficiently low so that the effect of density variations on the flow pattern is negligible), at  $c = c_1$ , starts to displace the indigenous unmarked water ( $c = c_o$ ) in the column. Let the tracer concentration,  $c = c(t)$ , be measured in the effluent leaving the column and presented in a graphical form, called a *breakthrough curve*, as a relationship between the relative tracer concentration,  $\epsilon (\equiv (c(t) - c_o)/(c_1 - c_o))$  and time. In the absence of dispersion, the breakthrough curve would take the form of the dashed line shown in Fig. 7.1.2, where  $\mathcal{U}_{\text{column}}$  is the pore volume in the column. This would be indicative of the movement of a persistent sharp front between the labeled and unlabeled fluids. In reality, due to hydrodynamic dispersion, the breakthrough curve will take the form of the *S-shaped curve* shown as a solid line in the figure.



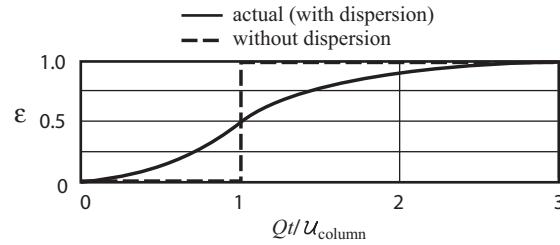


Figure 7.1.2: Breakthrough curve in one-dimensional flow in a column of homogeneous porous material;  $\varepsilon \equiv (c(t) - c_o)/(c_1 - c_o)$

As stated above, we cannot explain all the above observations on the basis of the average flow velocity. We must refer to what happens at the *microscopic level*, viz., *inside* the REV. There, we observe (Fig. 7.1.3) velocity variations in both magnitude and direction across any pore cross-section (even when the averaged flow is uniform), and between flow paths. We recall that even in a straight circular capillary tube, we have a parabolic distribution of fluid velocity (see any text on fluid mechanics), with zero velocity at the (stationary) solid surface, and a maximum velocity at the center of the tube. The void space may be visualized as an assembly of interconnected tubes, with varying diameters. The maximum velocity itself varies according to the size and shape of the pores. Because of the shape of the interconnected pore space, the (microscopic) streamlines deviate from the mean direction of flow (Fig. 7.1.3a and b). Altogether, we note that the velocity at the microscopic level varies in magnitude and direction from point to point within the fluid present in the void space. As a consequence, any initial cloud of closely-spaced tracer particles will spread out, with each fluid particle traveling along its own microscopic streamline. Therefore, the shape of the initial cloud will gradually change, and so will the fluid volume occupied by it. This phenomenon is referred to as *mechanical dispersion*, where the term ‘mechanical’ is used to remind us that this part of the spreading is due to fluid mechanical phenomena, and ‘dispersion’ is just another word for ‘spreading.’

As flow continues, the tracer particles, which originate from any small subdomain in the fluid within the void space, will occupy an ever growing volume of the flow domain. The two basic factors that produce mechanical dispersion are, therefore, *flow* and the *presence of a pore system* through which the flow takes place.

Although this spreading is in both the longitudinal direction, viz., that of the (local) average flow, and in the direction transverse to the latter, it is primarily in the former direction. Very little spreading in the direction perpendicular to the average flow is produced by velocity variations alone. Also, such velocity variations alone cannot explain the ever-growing width

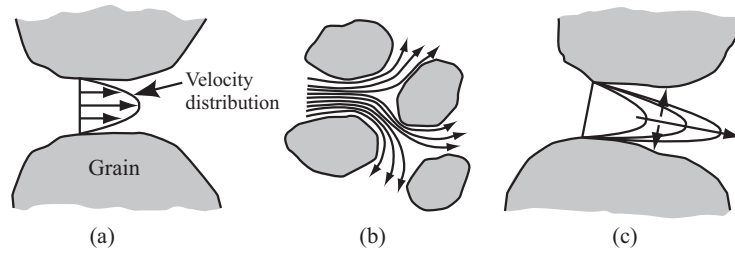


Figure 7.1.3: Dispersion due to mechanical spreading (a,b), and molecular diffusion (c).

(normal to the direction of flow) of a plume of tracer-labeled fluid particles originating at a point source.

In order to explain the observed spreading, especially transverse to the flow direction, we must refer to an additional phenomenon that takes place in the void space, viz., *molecular diffusion*, discussed in Subs. 7.1.3.

As shown in Subs. 7.1.3, molecular diffusion of a component in a fluid, caused by the random motion of the molecules (Brownian motion), produces an additional flux of the component's particles (at the microscopic level) from regions of higher concentrations to those of lower ones. This flux is relative to the advective one, produced by the velocity of the fluid phase. This means, for example, that as component particles spread *along* each microscopic stream-tube, as a result of mechanical dispersion, a concentration gradient is produced, which, in turn, produces an additional flux of the component by the mechanism of molecular diffusion. The latter phenomenon tends to equalize the concentration along every microscopic stream-tube. At the same time, a concentration gradient is also produced between adjacent stream-tubes, causing *lateral molecular diffusion, across streamlines* (Fig. 7.1.3c), which tends to equalize the concentration *across* pores. It is this phenomenon, combined with the randomness of the streamlines, that explains the observed ever-growing extent of transverse dispersion.

Thus, the deviations in solute concentration within a fluid phase, from the concentrations obtained by assuming advection only (at the average velocity), are due to two *simultaneous* phenomena: variations in the microscopic velocity of the phase, with respect to the averaged velocity, and molecular diffusion. In this way, molecular diffusion contributes to the dispersive flux. This contribution is *in addition* to the diffusive flux *at the macroscopic level*, as described by (the averaged) Fick's law. The latter is the only flux that takes place when the averaged velocity is zero. It may thus be concluded, that 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.

Molecular diffusion makes dispersion, even in purely laminar flow, an *irreversible* phenomenon. Irreversibility is exhibited, for example, by the growing width of a transition zone around an initially sharp tracer front in uniform flow, as the direction of the flow is reversed. A second source of irreversibility arises from the procedure used for averaging microscopic velocities, for example, averaging over an REV. There is an inevitable continual and growing loss of information at the microscopic level as one solves the governing equations at the macroscopic level forward in time. This fact exhibits itself in the smearing of an initially sharp macroscopic concentration front. This loss of information is irretrievable and, hence, the solutions to the equations are also not reversible. Thus, it is possible for macroscopic theories to be irreversible even without considering molecular diffusion. Whereas the first type of irreversibility, i.e., that caused by molecular diffusion, predicts the irreversibility of physical observable values (i.e., actual concentrations), the second type of irreversibility is manifested in the mathematical equations describing the dispersion phenomena.

We refer to the flux that causes mechanical dispersion (of a component) as *dispersive flux*. It is a *macroscopic* flux that takes into account the effect of the variations in the microscopic velocity in the vicinity of a 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 averaging process that we have chosen to employ.

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. An exception is in the absence of motion, when only molecular diffusion takes place. Because molecular diffusion is a relatively slow process, its overall effect on dispersion is more significant at low velocities.

In general, variations in tracer concentration cause changes in the fluid's density and viscosity. These, in turn, affect the flow regime (i.e., velocity distribution) that depends on these properties. We use the term *ideal tracer* when the concentration of the latter does not affect the fluid's density and viscosity. At relatively low concentrations, the ideal tracer approximation is sufficient for most practical purposes. However, in certain cases, for example, in the case of seawater intrusion into a region of freshwater, the density may vary appreciably, and the ideal tracer approximation should not be used; we have to take into account the effect of concentration changes on the fluid's density and viscosity.

#### 7.1.5 Dispersive flux

From the discussion in previous subsection, it follows that the dispersive flux, as a macroscopic flux of a component relative to the flux carried by the average velocity ( $\equiv$  advective flux), is a consequence of the fact that

both the velocity and the concentration vary from point to point within a fluid phase that occupies the entire void space, or part of it. Let us relate this flux to measurable quantities such as (average) velocity and (average) concentration. For the sake of simplicity, we shall make use of the volume averaging approach.

The advective flux of a component (per unit area of fluid) at a (microscopic) point,  $\mathbf{x}'$ , within a fluid phase ( $f$ ) 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 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:

$$\begin{aligned}\mathbf{V}(\mathbf{x}', t; \mathbf{x}) &= \overline{\mathbf{V}}^f(\mathbf{x}, t) + \overset{\circ}{\mathbf{V}}(\mathbf{x}', t; \mathbf{x}), \\ c(\mathbf{x}', t; \mathbf{x}) &= \overline{c}^f(\mathbf{x}, t) + \overset{\circ}{c}(\mathbf{x}', t; \mathbf{x}).\end{aligned}\quad (7.1.28)$$

Because an average value is constant over the REV, we have  $\overline{(\overset{\circ}{\cdot})^f}^f = \overline{(\cdot)}^f$ . As a consequence,

$$\overline{\overset{\circ}{\mathbf{V}}}^f = 0, \quad \text{and} \quad \overline{\overset{\circ}{c}}^f = 0. \quad (7.1.29)$$

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

$$\overline{c\mathbf{V}}^f = \overline{(\overline{c}^f + \overset{\circ}{c})(\overline{\mathbf{V}}^f + \overset{\circ}{\mathbf{V}})}^f = \overline{\overline{c}^f \overline{\mathbf{V}}^f}^f + \overline{\overline{c}^f \overset{\circ}{\mathbf{V}}}^f + \overline{\overset{\circ}{c} \overline{\mathbf{V}}^f}^f + \overline{\overset{\circ}{c} \overset{\circ}{\mathbf{V}}}^f. \quad (7.1.30)$$

Because the average of the deviations vanishes, the second and third terms on the right-hand side of (7.1.30) vanish, leaving the relationship:

$$\overline{c\mathbf{V}}^f = \overline{c}^f \overline{\mathbf{V}}^f + \overline{\overset{\circ}{c} \overset{\circ}{\mathbf{V}}}^f. \quad (7.1.31)$$

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

- an advective flux,  $\overline{c}^f \overline{\mathbf{V}}^f$ , expressing the mass of the component carried by the fluid at the latter's average velocity,  $\overline{\mathbf{V}}^f$ . The (microscopic) mass averaged velocity,  $\mathbf{V}$  was introduced in Subs. 7.1.3, and
- 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 point,  $\mathbf{x}$ , serves as a centroid. Recalling the discussion in the previous subsection, this is the flux that produces the mechanical spreading ( $\equiv$  the dispersion) of the component. We refer to it as the *dispersive flux*. It is a macroscopic flux caused by the variations in the microscopic fluid velocity and in fluid concentration in the vicinity of a (macroscopic) point in a porous medium domain. This flux is introduced

to circumvent the lack of information concerning the detailed velocity variations at the microscopic level. This lack of information is the consequence of our ignorance as to the detailed geometry of the surfaces that bound the fluid phase.

### 7.1.6 Dispersion coefficient and dispersivity

Our next objective is to express the dispersive flux in terms of averaged (and *measurable*) quantities, such as averaged velocity and averaged concentration. Investigations over a period of about three decades, starting around the mid-50's (e.g., de Josselin de Jong, 1958; Saffman, 1959; Bear, 1961a; Scheidegger, 1961; Bear, 1972; and Bear and Bachmat, 1990, p. 401), have led to the conclusion that the dispersive flux of a component (per unit area of fluid) in a porous medium can be expressed as a *Fickian-type* law (i.e., a law that resembles Fick's (linear) law of molecular diffusion) in the form:

$$\mathbf{J}^* \equiv \overline{\mathbf{c}\mathbf{V}}^f = -\mathbf{D} \cdot \nabla \bar{c}^f, \quad (7.1.32)$$

or, in indicial notation:

$$J_i^* \equiv \overline{cV_i}^f = -D_{ij} \frac{\partial \bar{c}^f}{\partial x_j}, \quad (7.1.33)$$

where the  $D_{ij}$ 's (dims.  $L^2/T$ ) are components of a coefficient,  $\mathbf{D}$ , called the *coefficient of mechanical (or advective) dispersion*, or the *dispersion coefficient*. This coefficient is a second rank tensor that relates the flux vector  $\mathbf{J}^*$  to the driving force vector  $-\nabla \bar{c}^f$ . Equation (7.1.33) is valid for the general case of an anisotropic porous medium. The dispersion coefficient is characterized by:

- The  $D_{ij}$ -matrix is *non-negative definite* (or positive definite). This is a consequence of thermodynamics: the *rate of entropy production*,  $\dot{S}$ , is related to the thermodynamic driving force,  $\mathbf{X}$ , and the thermodynamic flux,  $\mathbf{Y}$ , (referred to by De Groot and Mazur (1962) as *conjugated flux and force*, respectively) by  $\dot{S} = Y_i X_i$ . Here, the driving force  $\mathbf{X}$  is proportional to the negative concentration gradient,  $-\nabla \bar{c}^f$ . In this case, the rate of entropy production can be expressed by

$$\dot{S} = \chi \left( -D_{ij} \frac{\partial \bar{c}^f}{\partial x_j} \right) \times \chi \left( -\frac{\partial \bar{c}^f}{\partial x_i} \right) \geq 0, \quad \text{or} \quad \chi^2 D_{ij} \frac{\partial \bar{c}^f}{\partial x_j} \frac{\partial \bar{c}^f}{\partial x_i} \geq 0, \quad (7.1.34)$$

in which,  $\mathbf{Y} = \chi \mathbf{J}^* = -\chi \mathbf{D} \cdot \nabla \bar{c}^f$  and  $\mathbf{X} = -\chi \nabla \bar{c}^f$ . In the above,  $\chi$  is a parameter that depends on the extensive quantity considered; for each such quantity, it transforms the flux and the driving force, in the form of a gradient of an appropriate scalar considered (here  $\nabla \bar{c}^f$ ), into conjugated thermodynamic flux and force (De Groot and Mazur, 1962).

- The  $D_{ij}$ -matrix is *symmetric*, i.e.,

$$D_{ij} = D_{ji}. \quad (7.1.35)$$

This is a consequence of the conjugated force and flux relation (De Groot and Mazur, 1962), i.e., they satisfy

$$\frac{\partial Y_i}{\partial X_j} = \frac{\partial Y_j}{\partial X_i}. \quad (7.1.36)$$

Because we have circumvented the need to know the details (of velocity and concentration) at the microscopic level by ‘escaping’ to the macroscopic level, we are left with the need to determine a set of coefficients, in this case,  $D_{ij}$ . This situation is always the case whenever we try to overcome the lack of information about details at the microscopic level by moving to the macroscopic level.

It is interesting to note that although Darcy’s law, (4.1.27), and the Fick’s type law that governs the dispersive flux, (7.1.33), look similar, there is a basic difference between the coefficients  $K_{ij}$  and  $D_{ij}$ : the former is a function of the microscopic geometry of the void space (and of fluid properties), while the latter depends also on the macroscopic velocity field.

Several authors (e.g., Nikolaevskii, 1959; Bear, 1961a; Scheidegger, 1961; Bear and Bachmat, 1967, 1990) have derived the following expression for the components  $D_{ij}$ :

$$D_{ij} = a_{ijkl} \frac{\overline{V}_k^f \overline{V}_\ell^f}{\overline{V}^f} f(\text{Pe}, r), \quad (7.1.37)$$

where  $\overline{V}^f$  ( $\equiv |\overline{\mathbf{V}}^f|$ ) is the magnitude of the average velocity,  $r$  represents the ratio between characteristic lengths, in the direction of the flow and normal to it, within a pore, and  $\text{Pe}$  is a *Peclet number* defined by:

$$\text{Pe} \equiv \frac{\overline{V}^f \Delta_f}{\mathcal{D}_f}, \quad (7.1.38)$$

which expresses the ratio between the rates of transport of the considered component, respectively, by advection and by diffusion (see a detailed discussion on dimensionless numbers in Subs. 7.7). In this definition,  $\Delta_f$  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. Bear and Bachmat (1990) suggested an expression for  $f(\text{Pe}, r)$ . However, as is common in practice, we shall assume  $f(\text{Pe}, r) \approx 1$ , so that the coefficient of dispersion is expressed in the form

$$D_{ij} = a_{ijkl} \frac{V_k V_\ell}{V}, \quad (7.1.39)$$

in which  $V_k \equiv \overline{V}_k^f$ . Henceforth, for simplicity, we shall continue to drop the notation for intrinsic phase averaging.

The coefficients  $\mathbf{a}_{ijkl}$  (dims. L) appearing in (7.1.39) are components of a fourth rank tensor,  $\mathbf{a}$ , called the *dispersivity* of the porous medium. It expresses the effect, on the flow, of the microscopic configuration of the interface between the considered fluid phase and all other phases within the REV. In a saturated system, this interface is that between the fluid and the solid. When a fluid occupies only part of the void space, each of the dispersivity components,  $\mathbf{a}_{ijkl}$ , is a function of the volumetric fraction of the fluid.

In a three-dimensional space, the dispersivity tensor,  $\mathbf{a}_{ijkl}$ , has  $3^4 = 81$  components. However, because of various symmetry considerations, the number of independent coefficients is smaller. Specifically,

- (a) From the expression for the rate of entropy production,  $\dot{S}$ , and following the discussion leading to (7.1.34), we have

$$\dot{S} = \chi \left( -D_{ij} \frac{\partial \bar{c}^f}{\partial x_i} \right) \times \chi \left( -\frac{\partial \bar{c}^f}{\partial x_j} \right) = \chi^2 \mathbf{a}_{ijkl} \frac{\partial \bar{c}^f}{\partial x_i} \frac{\partial \bar{c}^f}{\partial x_j} \frac{V_k V_l}{V} \geq 0. \quad (7.1.40)$$

It follows that  $\mathbf{a}_{ijkl}$  is positive definite. This means that all *principal minors* of  $\mathbf{a}_{ijkl}$  are positive.

- (b) The values of the  $\mathbf{a}_{ijkl}$  are invariant under the permutation of indices,

$$\mathbf{a}_{ijkl} = \mathbf{a}_{ijlk}, \quad \mathbf{a}_{ijkl} = \mathbf{a}_{jikl}. \quad (7.1.41)$$

Hence, only 36 of the 81 components are *independent* of each other. It is interesting to note that the 36 components are constrained by  $2^6 - 1 = 63$  constraints. As the material has more symmetry properties, the number of independent coefficients decreases, until, when the material is isotropic, this number is reduced to two (Bear *et al.*, 2009).

### A. Isotropic porous medium

In an *isotropic porous medium*, it has been demonstrated (Bear and Bachmat, 1990; see also Sirotnine and Chaskolskaya, 1984, p. 651–2) that the 36 independent components reduce to *two*. This can be shown by considering fourth rank tensors that satisfy the relationships (7.1.41) and are invariant under the action of full rotational (orthogonal) symmetry. The two coefficients are designated as  $\mathbf{a}_L$  and  $\mathbf{a}_T$ , and are called the *longitudinal* and the *transverse dispersivities* of the porous medium, respectively. The parameter  $\mathbf{a}_L$  is a length that characterizes the microscopic configuration of the phase within the REV. Thus, for a phase that completely fills the void space in a porous medium,  $\mathbf{a}_L$  should be of the order of magnitude of the size of a typical pore. Furthermore, by the positive definiteness of  $\mathbf{a}_{ijkl}$ , it follows that

$$\mathbf{a}_L \geq 0, \quad \mathbf{a}_T \geq 0. \quad (7.1.42)$$

De Josselin de Jong (1958) and laboratory column experiments (e.g., Bear, 1961b) have shown that  $\mathbf{a}_T$  is 8 to 24 times smaller than  $\mathbf{a}_L$ .

In terms of  $\mathbf{a}_L$  and  $\mathbf{a}_T$ , components of the dispersivity tensor for an *isotropic porous medium* can be expressed in the form:

$$\mathbf{a}_{ikj\ell} = \mathbf{a}_T \delta_{ij} \delta_{k\ell} + \frac{\mathbf{a}_L - \mathbf{a}_T}{2} (\delta_{ik} \delta_{j\ell} + \delta_{i\ell} \delta_{jk}), \quad (7.1.43)$$

where  $\delta_{ij}$  is the Kronecker delta. The coefficient of dispersion, with  $f(\text{Pe}, r) \simeq 1$ , can then be expressed as

$$\mathbf{D}_{ij} = \left[ \mathbf{a}_T \delta_{ij} + (\mathbf{a}_L - \mathbf{a}_T) \frac{V_i V_j}{V^2} \right] V, \quad V = |\mathbf{V}|, \quad (7.1.44)$$

in which  $V_i$  denotes the  $i$ th component of the average velocity vector  $\mathbf{V}$ .

In Cartesian coordinates, with  $V_x$ ,  $V_y$ , and  $V_z$  denoting average velocity components in the  $x$ ,  $y$ , and  $z$  directions, respectively, we obtain from (7.1.44):

$$\begin{aligned} \mathbf{D}_{xx} &= \left[ \mathbf{a}_T + (\mathbf{a}_L - \mathbf{a}_T) \frac{V_x^2}{V^2} \right] V = \frac{1}{V} (\mathbf{a}_L V_x^2 + \mathbf{a}_T V_y^2 + \mathbf{a}_T V_z^2), \\ \mathbf{D}_{yy} &= \left[ \mathbf{a}_T + (\mathbf{a}_L - \mathbf{a}_T) \frac{V_y^2}{V^2} \right] V = \frac{1}{V} (\mathbf{a}_T V_x^2 + \mathbf{a}_L V_y^2 + \mathbf{a}_T V_z^2), \\ \mathbf{D}_{zz} &= \left[ \mathbf{a}_T + (\mathbf{a}_L - \mathbf{a}_T) \frac{V_z^2}{V^2} \right] V = \frac{1}{V} (\mathbf{a}_T V_x^2 + \mathbf{a}_T V_y^2 + \mathbf{a}_L V_z^2), \\ \mathbf{D}_{xy} &= \left[ (\mathbf{a}_L - \mathbf{a}_T) \frac{V_x V_y}{V^2} \right] V = \mathbf{D}_{yx}, \\ \mathbf{D}_{xz} &= \left[ (\mathbf{a}_L - \mathbf{a}_T) \frac{V_x V_z}{V^2} \right] V = \mathbf{D}_{zx}, \\ \mathbf{D}_{yz} &= \left[ (\mathbf{a}_L - \mathbf{a}_T) \frac{V_y V_z}{V^2} \right] V = \mathbf{D}_{zy}. \end{aligned} \quad (7.1.45)$$

Like any second rank tensor,  $\mathbf{D}$  also has *three principal directions*. Using these principal directions as Cartesian coordinate axes,  $x_1, x_2, x_3$ , we may write  $\mathbf{D}$ , in the matrix form:

$$\mathbf{D} = \begin{bmatrix} \mathbf{D}_{x_1 x_1} & 0 & 0 \\ 0 & \mathbf{D}_{x_2 x_2} & 0 \\ 0 & 0 & \mathbf{D}_{x_3 x_3} \end{bmatrix}. \quad (7.1.46)$$

In the special case of uniform flow, say  $V_x = V$ ,  $V_y = V_z = 0$ , equation (7.1.45) reduces to  $\mathbf{D}_{xx} = \mathbf{a}_L V$ ,  $\mathbf{D}_{yy} = \mathbf{a}_T V$ ,  $\mathbf{D}_{zz} = \mathbf{a}_T V$ ,  $\mathbf{D}_{xy} = \mathbf{D}_{xz} = \mathbf{D}_{yz} = 0$ ; or, in matrix form:

$$\mathbf{D} = \begin{bmatrix} \mathbf{a}_L & 0 & 0 \\ 0 & \mathbf{a}_T & 0 \\ 0 & 0 & \mathbf{a}_T \end{bmatrix} V = \begin{bmatrix} \mathbf{D}_L & 0 & 0 \\ 0 & \mathbf{D}_T & 0 \\ 0 & 0 & \mathbf{D}_T \end{bmatrix}, \quad (7.1.47)$$



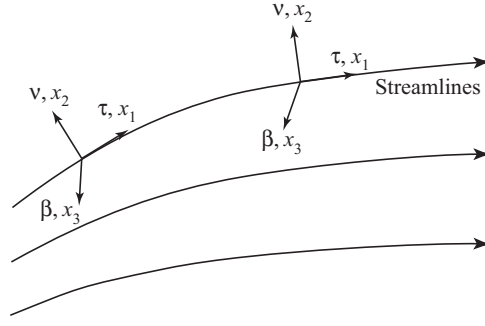


Figure 7.1.4: Principal directions of dispersion coefficient in an isotropic porous medium.

where  $D_L$  and  $D_T$  are, respectively, the longitudinal and transversal dispersion coefficients of an isotropic porous medium.

We have already mentioned that the tensor  $\mathbf{D}$  (and 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,  $\boldsymbol{\tau}$ , in the direction of the *tangent* to the streamline, (i.e., in the direction of the flow),
- a unit vector,  $\boldsymbol{\nu}$ , called the *principal normal* to the streamline (defined by  $\kappa\boldsymbol{\nu} = d\boldsymbol{\tau}/ds$ , where  $s$  is the distance measured along the streamline, and  $\kappa$  is the curvature of the streamline at the point), and
- a unit vector,  $\boldsymbol{\beta}$  ( $= \boldsymbol{\tau} \times \boldsymbol{\nu}$ ), normal to both  $\boldsymbol{\tau}$  and  $\boldsymbol{\nu}$  (Fig. 7.1.4).

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 vary from point to point and in time.

If, *locally*, we select  $\boldsymbol{\tau}$ ,  $\boldsymbol{\nu}$  and  $\boldsymbol{\beta}$ , as *basis vectors* of the coordinate system,  $x_1, x_2, x_3$ , then  $\mathbf{D}$  takes the form (7.1.46). 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 transverse dispersion*.

## B. Transverse isotropy (axial symmetry)

In an *anisotropic porous medium*, the number of independent dispersivity coefficients is larger, depending on the kind of symmetry exhibited by the anisotropic medium. As an example, we may consider a porous medium with *transverse isotropy*, i.e., a porous medium with one axis of rotational symmetry. This means that in any plane perpendicular to that axis, the material is isotropic, i.e., it does not exhibit property changes with direction, while medium properties in the direction parallel to this axis are different (see Sec. 2.5).

For an axially symmetrical porous medium, with the vector  $\mathbf{e}$  (components  $e_i$ ) indicating the axis of symmetry, there exist *six* independent  $\mathbf{a}_{ijkl}$ -coefficients. The dispersivity components can then be expressed by (Bear *et al.*, 2009)

$$\begin{aligned} \mathbf{a}_{ijkl} = & \mathbf{a}_1 \delta_{ij} \delta_{kl} + \frac{\mathbf{a}_2}{2} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) + \mathbf{a}_3 e_i e_j \delta_{kl} + \mathbf{a}_4 e_k e_l \delta_{ij} \\ & + \frac{\mathbf{a}_5}{2} (e_i e_k \delta_{jl} + e_j e_k \delta_{il} + e_i e_l \delta_{jk} + e_j e_l \delta_{ik}) + \mathbf{a}_6 e_i e_j e_k e_l, \end{aligned} \quad (7.1.48)$$

with  $\mathbf{a}_1$  through  $\mathbf{a}_6$  indicating the six independent dispersivity coefficients. Fel and Bear (2009) determined the constraints that the six  $\mathbf{a}_i$ 's have to satisfy as a consequence of the positive definiteness of the entropy production, expressed by (7.1.34). We note that by dropping terms associated with  $e_i$  in (7.1.48), we obtain the isotropic case, described by (7.1.43), i.e., with  $\mathbf{a}_1 = \mathbf{a}_T$ , and  $\mathbf{a}_2 = \mathbf{a}_L - \mathbf{a}_T$ , and  $\mathbf{a}_3 = \mathbf{a}_4 = \mathbf{a}_5 = \mathbf{a}_6 = 0$ . These six dispersivity coefficients,  $\mathbf{a}_1$ – $\mathbf{a}_6$ , are *properties of the porous medium only*, meaning that they are independent of the flow taking place in the porous medium, and the chosen coordinate system.

Based on (7.1.39), the corresponding expression for the dispersion coefficients  $\mathbf{D}_{ij}$  is

$$\begin{aligned} \mathbf{D}_{ij} = & \left[ \mathbf{a}_1 \delta_{ij} + \mathbf{a}_2 \frac{V_i V_j}{V^2} + \mathbf{a}_3 e_i e_j + \mathbf{a}_4 \delta_{ij} \frac{(V_k e_k)^2}{V^2} \right. \\ & \left. + \mathbf{a}_5 \frac{V_k e_k}{V} \frac{V_i e_j + V_j e_i}{V^2} + \mathbf{a}_6 e_i e_j \frac{(V_k e_k)^2}{V^2} \right] V. \end{aligned} \quad (7.1.49)$$

We note that the dispersion coefficient, which is used for determining the dispersive flux by means of (7.1.32), depends not only on the porous medium (through the dispersivity coefficients), but also on the velocity vector. As velocity may vary in space and time, so does the dispersion coefficients.

In order to model solute transport in a transversely isotropic porous medium under general flow conditions, we need to determine the *six* independent dispersivities, or dispersivity coefficients. These  $\mathbf{a}_i$  coefficients can be determined by conducting tracer tests in the field, and comparing tracer concentrations within a plume with available analytical or numerical solutions. Generally, this parameter determination is conducted as an inverse solution procedure in which the optimal solution is obtained by minimizing the sum of square errors between the observed and theoretically predicted concentrations (Sec. 11.3).

As the expression for dispersive flux, (7.1.32), and the solute transport equation (7.2.23) introduced in Sub. 7.2.2, involve six dispersion coefficients  $\mathbf{D}_{ij}$  (six, instead of nine, because of the symmetry  $\mathbf{D}_{ij} = \mathbf{D}_{ji}$ ), the first step in a parameter estimation procedure is to determine these six components of the dispersion coefficient. Given a transversely isotropic aquifer with known axis of symmetry (i.e, known vector components  $e_i$ ), and known flow (i.e.,

known  $V_i$ ), in principle, it is possible to determine the dispersion coefficients from information on observed concentrations during a controlled experiment.

Once the six dispersion components  $D_{ij}$  have been determined for a given location through such experiments, the next step is to solve the following linear system of equations, based on (7.1.49), for the six coefficients,  $\mathbf{a}_1$ – $\mathbf{a}_6$ ,

$$[\mathbf{EV}] \begin{Bmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \\ \mathbf{a}_4 \\ \mathbf{a}_5 \\ \mathbf{a}_6 \end{Bmatrix} = \begin{Bmatrix} D_{11} \\ D_{22} \\ D_{33} \\ D_{12} \\ D_{13} \\ D_{23} \end{Bmatrix}, \quad (7.1.50)$$

in which  $[\mathbf{EV}]$  is a  $6 \times 6$  matrix containing the expressions of  $e_i$  and  $V_i$ , as defined in (7.1.49). However, a matrix analysis shows that the matrix  $[\mathbf{EV}]$  is of rank four, meaning that of the six equations defined in (7.1.50) (or (7.1.49)), only four are *linearly independent*, and the other two are linearly dependent on the rest. This means that (7.1.50) can yield at most four  $a_i$  values.

While the above conclusion has been proven for the general case of any orientation of coordinate system, it is of interest to examine some special cases. In the case of a horizontally layered material, selecting the  $z$ -axis to coincide with the axis of material symmetry, i.e.,  $e_3 = 1$  and  $e_1 = e_2 = 0$ , we express (7.1.49) as

$$\begin{aligned} D_{xx} &= \left( \mathbf{a}_1 + \mathbf{a}_2 \frac{V_x^2}{V^2} + \mathbf{a}_4 \frac{V_z^2}{V^2} \right) V, \\ D_{yy} &= \left( \mathbf{a}_1 + \mathbf{a}_2 \frac{V_y^2}{V^2} + \mathbf{a}_4 \frac{V_z^2}{V^2} \right) V, \\ D_{zz} &= \left[ \mathbf{a}_1 + \mathbf{a}_3 + (\mathbf{a}_2 + \mathbf{a}_4 + 2\mathbf{a}_5 + \mathbf{a}_6) \frac{V_z^2}{V^2} \right] V, \\ D_{xy} = D_{yx} &= \mathbf{a}_2 \frac{V_x V_y}{V^2} V, \\ D_{xz} = D_{zx} &= (\mathbf{a}_2 + \mathbf{a}_5) \frac{V_x V_z}{V^2} V, \\ D_{yz} = D_{zy} &= (\mathbf{a}_2 + \mathbf{a}_5) \frac{V_y V_z}{V^2} V. \end{aligned} \quad (7.1.51)$$

By eliminating the factor  $(\mathbf{a}_2 + \mathbf{a}_5)$  between the fifth and sixth equations in (7.1.51), we can clearly see that  $D_{xz}$  and  $D_{yz}$  are related to each other. Further analysis shows that the matrix is of rank four, and the following constraints must be satisfied in order for the system of equations to have a solution:

$$\begin{aligned} D_{yz} &= \frac{V_y}{V_x} D_{xz}, \\ D_{xx} &= D_{yy} + \frac{V_x^2 - V_y^2}{V_x V_y} D_{xy}. \end{aligned} \quad (7.1.52)$$

Hence, *only four of the six dispersion coefficients are independent.*

Often, it is convenient to use a *local coordinate system* that coincides with the flow direction at the considered location. For example, in the case of uniform flow in the direction of the  $x_1$ -axis (see Fig. 7.1.4), such that  $V_1 = V$  and  $V_2 = V_3 = 0$ , we can show the following interdependence among dispersion coefficients:

$$\begin{aligned} D_{xy} &= \frac{e_y}{e_z} D_{xz}, \\ D_{yy} &= D_{zz} + \frac{e_y^2 - e_z^2}{e_y e_z} D_{yz}. \end{aligned} \quad (7.1.53)$$

This is the same conclusion as the above, that is, only four of the dispersion coefficients are independent.

The important conclusions of the above analysis are:

- (a) In a single field experiment, in which the flow conditions remain unchanged, it is possible to determine only four dispersion coefficients at any one location, due to the required interdependency given either by (7.1.52) or by (7.1.53).
- (b) Given these four independent dispersion coefficients, it is not possible to resolve the six dispersivity coefficients,  $a_1$ – $a_6$ , from (7.1.50), due to the rank deficiency of the matrix.
- (c) However, as demonstrated below (see also Fel and Bear, 2009), it is possible to determine the six dispersivity coefficients if two experiments are conducted.
- (d) In a forward modeling problem, in which values of six dispersion coefficients are required as input, one needs to check the consistency of the assigned dispersion values. These values need to be either determined from (7.1.49), based on the six dispersivity coefficients, or satisfy the relations as shown in (7.1.52) or (7.1.53).

Next, let us consider two special flow cases in the layered medium considered above. In the following discussion, we shall choose the  $z$ -axis to coincide with the material axis of symmetry, i.e.,  $e_3 = 1$  and  $e_1 = e_2 = 0$ .

In the first case, we consider uniform flow *normal* to the layers, that is, in the  $z$ -direction, such that  $V_3 = V$  and  $V_1 = V_2 = 0$ . Using this condition in (7.1.49), we obtain

$$\mathbf{D}^V = \begin{bmatrix} \mathbf{a}_{TH}^V & 0 & 0 \\ 0 & \mathbf{a}_{TH}^V & 0 \\ 0 & 0 & \mathbf{a}_{LV}^V \end{bmatrix} V, \quad \begin{aligned} \mathbf{a}_{TH}^V &= \mathbf{a}_1 + \mathbf{a}_4, \\ \mathbf{a}_{LV}^V &= \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3 + \mathbf{a}_4 + 2\mathbf{a}_5 + \mathbf{a}_6, \end{aligned} \quad (7.1.54)$$

where the superscript  $(.)^V$  is used to emphasize that the flow direction is vertical,  $\mathbf{a}_{TH}^V$  is the transverse dispersivity in the horizontal direction (only one value because of the isotropy in the horizontal plane), and  $\mathbf{a}_{LV}^V$  is the longitudinal dispersivity in the vertical direction. Altogether, to describe dispersion in a layered horizontal porous medium, when the flow is uniform and normal to the layers, we need only one longitudinal and one transversal dispersivities.

As a second case, we consider uniform flow *parallel* to the layers, say, in the  $+x$ -axis direction, such that  $V_1 = V$  and  $V_2 = V_3 = 0$ . Equation (7.1.49) becomes:

$$\mathbf{D}^H = \begin{bmatrix} \mathbf{a}_{LH}^H & 0 & 0 \\ 0 & \mathbf{a}_{TH}^H & 0 \\ 0 & 0 & \mathbf{a}_{TV}^H \end{bmatrix} V, \quad \begin{aligned} \mathbf{a}_{LH}^H &= \mathbf{a}_1 + \mathbf{a}_2, \\ \mathbf{a}_{TH}^H &= \mathbf{a}_1, \\ \mathbf{a}_{TV}^H &= \mathbf{a}_1 + \mathbf{a}_3, \end{aligned} \quad (7.1.55)$$

where  $\mathbf{a}_{TH}^H$  and  $\mathbf{a}_{TV}^H$  are, respectively, the transverse dispersivities in the horizontal and in the vertical directions, and  $\mathbf{a}_{LH}^H$  is the longitudinal dispersivity in the horizontal direction. Thus, to describe dispersion in a layered horizontal porous medium, when flow is uniform and parallel to the layers, we need one longitudinal and two transversal dispersivities.

As observed in the cases discussed above, under uniform flow conditions, we can only determine two, three, or four independent dispersion coefficients in a single experiment, depending on whether the flow is perpendicular, parallel, or at an angle, to the material symmetry axis. This implies that *at least two flow tests in different flow directions are needed, and one of the two directions must be inclined with respect to the direction of the material symmetry axis*. For example, if we conduct a horizontal flow test, and obtain result as in (7.1.55), we can determine three dispersivity coefficients,  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$ . For the second test, the flow should be neither in the vertical, nor in the horizontal, direction, as there will not be sufficient information to determine the remaining three coefficients. The flow of the second test must be in an inclined direction with the horizontal plane and the vertical axis, which will provide four additional equations. The remaining three coefficients can then be determined under overdeterminancy condition. Similar statement was presented by Fel and Bear (2009) for the special case of flow in the horizontal direction, and making a  $45^\circ$  angle with the axis of symmetry.

In the above, we have assumed that the direction of the axis of symmetry is known *a priori*, i.e., we know the three values:  $e_1$ ,  $e_2$  and  $e_3$  that appear in (7.1.49). If this direction is not known, we have to use the experimental data to solve the inverse problem also for two of these three components of  $\mathbf{e}$  (because  $e_1^2 + e_2^2 + e_3^2 = 1$ ), for a total of 8 unknown values. In this case, two flow tests in two different inclined directions (with respect to the materials axis of symmetry) are sufficient for the determination of these 8 unknowns.

### C. Anisotropy with tetragonal symmetry

As an example of such porous medium material, we may consider one that is made up of orderly packed solid boxes  $a \times a \times c$ , with equal spacing between

the boxes in all directions (or cubes with 3 different spaces). For this case, the 36 independent  $\mathbf{a}_{ijkl}$ -components can be expressed by 7 independent parameters, which are subject to certain constraints (Bear *et al.*, 2009). It is interesting to note that this case is not identical to the case with axial symmetry (such as a stratified aquifer), considered above. Here, we also need information on the directions in which the boxes,  $a \times a \times c$ , are positioned in space, e.g., in the form of two of the three  $e_i$ 's. This case is analyzed in detail by Bear *et al.* (2009).

#### D. Anisotropy with orthorhombic symmetry

An example is a porous medium material made up of orderly packed solid boxes  $a \times b \times c$  with equal spacing between the boxes in all directions (or cubes with three different spaces). For this case, the 36 independent dispersivity components can be expressed by *twelve* independent parameters. We also need information on the directions in which the boxes,  $a \times b \times c$ , are oriented in space (and this, as indicated earlier, requires information on two  $e_i$ 's).

It is possible to analyze three special cases of flow, each one with uniform flow parallel to one of the three axes. To describe dispersion in each of these three cases we need only three coefficients: a longitudinal dispersivity and two transversal ones.

In each of the material symmetry cases discussed above, the number of independent coefficients is accompanied by a number of constraints that these coefficients have to satisfy. The information concerning the number of independent coefficients and the constraints among them (Bear *et al.*, 2009) is important when experiments are conducted aimed at determining the values of these coefficients for a specific porous medium, by using an inverse method.

Similar to the discussion presented with respect to the experimental procedure for determining the dispersivity coefficients in the case of transverse isotropy, here also, a number of independent experiments will be required. Also, in practice, because of the inaccuracy and uncertainty in the measured values during experiments, (say of concentrations and piezometric heads) an optimization procedure that minimizes the overall error may be called for.

#### E. Other models for dispersion in anisotropic domains

Some authors, on the basis of field observations, have suggested that for flow parallel to the horizontal stratification in a stratified (= layered) aquifer, transverse dispersion is much smaller in the vertical direction than in the horizontal one, i.e.,  $\mathbf{a}_{TH}^H \gg \mathbf{a}_{TV}^H$  in (7.1.55) (Robson, 1974, 1978; Garabedian *et al.*, 1991; Gelhar *et al.*, 1992). Based on the above observation, Burnett and Frind (1987) (see also Jensen *et al.*, 1993; Zheng and Bennett, 1995) suggested a 'working model' for transversely isotropic porous medium, in which the dispersion tensor is defined by *three* dispersivities only (rather than six, see Subs. 7.1.6B): a longitudinal dispersivity,  $\mathbf{a}_L$ , and two transversal dispersivities, a horizontal one,  $\mathbf{a}_{TH}$ , and a vertical one,  $\mathbf{a}_{TV}$ . The components

of the dispersion tensor in three dimensions, with the  $z$ -axis as the axis of material symmetry, are presented as:

$$\begin{aligned}
 D_{xx} &= \frac{1}{V} (a_L V_x^2 + a_{TH} V_y^2 + a_{TV} V_z^2), \\
 D_{yy} &= \frac{1}{V} (a_{TH} V_x^2 + a_L V_y^2 + a_{TV} V_z^2), \\
 D_{zz} &= \frac{1}{V} (a_{TV} V_x^2 + a_{TV} V_y^2 + a_L V_z^2), \\
 D_{xy} &= D_{yx} = \frac{1}{V} (a_L - a_{TH}) V_x V_y, \\
 D_{xz} &= D_{zx} = \frac{1}{V} (a_L - a_{TV}) V_x V_z, \\
 D_{yz} &= D_{zy} = \frac{1}{V} (a_L - a_{TV}) V_y V_z.
 \end{aligned} \tag{7.1.56}$$

These expressions can be compared with those for the isotropic case, (7.1.45). Burnett and Frind (1987) further *assumed* that  $a_{TH} \gg a_{TV}$ . Most solute transport codes (Sec. 8.8), such as MT3D (Zheng, 1990), MOC3D (Konikow *et al.*, 1996), and PHAST (Parkhurst *et al.*, 2004), use this formulation. The relations presented in (7.1.56), however, are not consistent with (7.1.49). In fact, Lichtner *et al.* (2002, 2008) have demonstrated that (7.1.56) does not conform with tensor transformation rules, suggesting that it is not an acceptable model.

Based on a turbulence model investigated by Batchelor (1959), using a method introduced by Robertson (1940), Poreh (1965) suggested a model that is based on four dispersivity coefficients,

$$D_{ij} = \left[ \alpha_1 \delta_{ij} + \alpha_2 \frac{V_i V_j}{V^2} + \alpha_3 e_i e_j + \frac{\alpha_4}{2} \frac{e_i V_j + e_j V_i}{V} \right] V. \tag{7.1.57}$$

Comparing the above with (7.1.49), we observe that Poreh's (1965) model is equivalent to setting  $V_k e_k / V$  to zero for terms associated with  $a_4$  and  $a_6$ , and to 1 for the term associated with  $a_5$ . Here we notice that

$$\frac{V_k e_k}{V} = \frac{\mathbf{V} \cdot \mathbf{e}}{V} = \cos \theta, \tag{7.1.58}$$

where  $\theta$  is the angle between the material axis and the flow direction. A reason for the absence of such terms might be that the *turbulence* model lacks the *material anisotropy* aspect, because fluid as a material is *isotropic*; while in a porous medium we have the additional effect of material anisotropy, represented by the  $\cos \theta$  term.

Lichtner *et al.* (2002) examined the Poreh (1965) model and discussed the need for introducing  $\cos \theta$  as a factor in the constitutive model. As a result, a three parameter model (called a 'four parameter model' in Lichtner *et al.* (2002)) was proposed. By selecting  $z$  as the material axis of symmetry

( $e_3 = 1$ ,  $e_1 = e_2 = 0$ ), the components of the dispersion coefficient in Lichtner *et al.* (2002) model are

$$\begin{aligned}
 D_{xx} &= \left[ a_L \frac{V_x^2}{V^2} + a_{TH} \frac{V_y^2}{V_x^2 + V_y^2} + a_T \frac{V_x^2 V_z^2}{V^2(V_x^2 + V_y^2)} \right] V, \\
 D_{yy} &= \left[ a_L \frac{V_y^2}{V^2} + a_{TH} \frac{V_x^2}{V_x^2 + V_y^2} + a_T \frac{V_y^2 V_z^2}{V^2(V_x^2 + V_y^2)} \right] V, \\
 D_{zz} &= \left[ a_L \frac{V_z^2}{V^2} + a_T \frac{V_x^2 + V_y^2}{V^2} \right] V, \\
 D_{xy} = D_{yx} &= \left[ a_L \frac{V_x V_y}{V^2} + a_{TH} \frac{V_x V_y}{V_x^2 + V_y^2} + a_T \frac{V_x V_y V_z^2}{V^2(V_x^2 + V_y^2)} \right] V, \\
 D_{xz} = D_{zx} &= \left[ (a_L - a_T) \frac{V_x V_z}{V^2} \right] V, \\
 D_{yz} = D_{zy} &= \left[ (a_L - a_T) \frac{V_y V_z}{V^2} \right] V,
 \end{aligned} \tag{7.1.59}$$

where

$$\begin{aligned}
 a_L &= \alpha_1 + \alpha_2 - \alpha_3 \cos^2 \theta, \\
 a_T &= \alpha_1 + \alpha_3(1 - \cos^2 \theta), \\
 a_{TH} &= \alpha_1,
 \end{aligned} \tag{7.1.60}$$

with  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  as the three material coefficients (which are different from those defined in (7.1.57)). The relation (7.1.59) also shows that at any location in the flow field, only three of the dispersivity coefficients can be independent.

For vertical flow ( $\theta = 0$ ), (7.1.59) reduces to

$$D_{ij}^V = \begin{bmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_1 & 0 \\ 0 & 0 & \alpha_1 + \alpha_2 - \alpha_3 \end{bmatrix} V = \begin{bmatrix} a_{TH}^V & 0 & 0 \\ 0 & a_{TH}^V & 0 \\ 0 & 0 & a_{LV}^V \end{bmatrix} V, \tag{7.1.61}$$

and for horizontal flow ( $\theta = 90^\circ$ ),

$$D_{ij}^H = \begin{bmatrix} \alpha_1 + \alpha_2 & 0 & 0 \\ 0 & \alpha_1 & 0 \\ 0 & 0 & \alpha_1 + \alpha_3 \end{bmatrix} V = \begin{bmatrix} a_{LH}^H & 0 & 0 \\ 0 & a_{TH}^H & 0 \\ 0 & 0 & a_{TV}^H \end{bmatrix} V. \tag{7.1.62}$$

In the above, we observe

$$\begin{aligned}
 a_{LV}^V &= \alpha_1 + \alpha_2 + \alpha_3, & a_{LH}^H &= \alpha_1 + \alpha_2, \\
 a_{TV}^H &= \alpha_1 + \alpha_3, & a_{TH}^H &= a_{TH}^V = \alpha_1.
 \end{aligned} \tag{7.1.63}$$



We note that the dispersivities,  $a_{LV}^V$ ,  $a_{LH}^H$ , etc., defined above, are not the same as those in (7.1.54) and (7.1.55). From (7.1.61) and (7.1.62), we note the important consequence that  $D_{TH}^H = D_{TH}^V$ , i.e., the horizontal transverse dispersion coefficient of the horizontal flow is equal to the transverse dispersion coefficient of the vertical flow. We also note that  $D_{TV}^H = D_{LV}^V - D_{LH}^H + D_{TH}^H$ . In other words, if we conduct a horizontal and a vertical uniform flow tests, the dispersion coefficients obtained are related to each other.

## F. Additional comments on dispersion

Before leaving the discussion on the flux of a dissolved chemical species, let us mention a number of phenomena, which may further affect the spreading and travel time of solutes in porous media:

**Multiphase flow** In multiphase flow, a dispersivity is associated with each fluid phase. Thus, each of the dispersivity components, e.g., the longitudinal and transversal dispersivities, depends on the phase configuration within the void space. Hence, each of these components is a function of the phase saturation. However, very little information on these functions is available to date. Probably because of this reason, the dependence on saturation is usually overlooked in practice.

**Non-Fickian dispersion model** In recent years, several researchers (e.g., Berkowitz *et al.*, 2000, 2002; Berkowitz and Scher, 2001) have demonstrated that even in a relatively homogeneous porous medium, the dispersive flux cannot be expressed as a Fickian-type law.

Consider a solute slug injected into an aquifer with uniform flow. After waiting some initial short period, so that the use of the continuum approach will be justified, the tracer spreads out such that, in a Fickian model, contours of constant solute concentration can be described as confocal ellipsoids (in 3-D), indicating a binormal distribution. Such an experiment is shown, conceptually, in Fig. 7.1.1b. The *size* of the contaminant cloud, estimated by its longitudinal and transverse standard deviations,  $\sigma_L$ , and  $\sigma_T$ , respectively, grows with the square root of time

$$\sigma_L = \sqrt{2D_L t} = \sqrt{2D_L L/V}, \quad \text{and} \quad \sigma_T = \sqrt{2D_T t} = \sqrt{2D_T L/V}, \quad (7.1.64)$$

where  $L(= Vt)$  is the distance that the center of mass has traveled during time  $t$ , at the mean velocity  $V$ .

It is well known from the dispersion phenomena observed in pipe flow (Taylor, 1953, 1954), natural streams (Liu and Cheng, 1980), and groundwater flow, that at small times, the dispersion coefficient is not a constant; rather it grows with time and reaches a constant only after a sufficiently long time (or large distance traveled). Also, the concentration cloud is skewed toward the source, and becomes Gaussian only after a certain distance traveled. Other models based on laboratory observation and random walk models (Berkowitz *et al.*, 2000, 2002; Berkowitz and Scher, 2001) have indicated that the center

of mass of the cloud does not travel with the flow velocity, and  $L \sim t^\beta$ ,  $\sigma \sim t^\beta$ , where  $0 < \beta < 1$ . It is of interest to observe that for a Fickian model,  $L \sim t$ ,  $\sigma \sim t^{1/2}$ , and  $L/\sigma \sim t^{1/2}$ ; while for this non-Fickian model,  $L/\sigma \sim \text{constant}$ .

**Ion exclusion** Because of the electrical charge on certain solid surfaces, a chemical species that is an ion may be repelled from the solid wall of the void space, where the water velocity is small (recalling that we assume that water is adsorbed to the solid wall), and move mainly in the regions of higher velocity inside the void space. The average velocity of the water carrying and dispersing the species is, thus, higher than for non-ionic contaminants. As a consequence, the advective flux of the contaminant will be higher, and so will the coefficient of dispersion, which is proportional to the average velocity. This phenomenon has also been called *charge exclusion* (Gvirtzman and Magaritz, 1989; Gvirtzman and Gorelick, 1991).

**Size exclusion** Some molecules, or ions, are so large that their travel is restricted to the larger pores. As a consequence, they are carried (by advection) at a higher average water velocity. The higher average velocity also results in a higher coefficient of dispersion. This phenomenon is more prevalent in fine-grained soils and for large molecules, like organic macromolecules.

Although this section deals with a dissolved component, we would like also to point out that the magnitude of exclusion is particularly important when considering the transport of microorganisms and of colloidal particles that may carry contaminants, because of their relatively large size.

### 7.1.7 Total flux

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

$$\begin{aligned}\mathbf{J}_{\text{total}}^\gamma &= \bar{c}^f \bar{\mathbf{V}}^f + \mathbf{J}^\gamma + \mathbf{J}^{*\gamma} \\ &= \bar{c}^f \bar{\mathbf{V}}^f - \mathbf{D}_h^\gamma \cdot \nabla \bar{c}^f,\end{aligned}\quad (7.1.65)$$

where

$$\mathbf{D}_h^\gamma \equiv \mathbf{D} + \mathcal{D}^{*\gamma} \quad (7.1.66)$$

denotes the *coefficient of hydrodynamic dispersion* of the chemical species. Note that the average in  $\bar{c}^f$  is an intrinsic phase averages. Henceforth, we shall omit the symbol that denotes the intrinsic phase average.

### 7.1.8 Field-scale heterogeneity

In Subs. 7.1.4, the phenomenon of solute dispersion was shown to be a consequence of the heterogeneity of the porous medium *at the microscopic scale*, i.e., due to the presence of a solid matrix and a void space within the REV. A grain or pore diameter, or the hydraulic radius of the pore space, was

suggested as the *scale* of this heterogeneity. This heterogeneity produces the velocity variations that take place inside the void space. The dispersive flux, a macroscopic level concept obtained by averaging over an REV, was 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.

As emphasized in Subs. 1.3.4, subsurface domains, which are the porous medium domains of interest in this book, are highly heterogeneous with respect to their macroscopic coefficients, e.g., porosity and permeability. We have introduced the term ‘megascopic level’, obtained by smoothing out variations at the macroscopic level, and introduced the concept of ‘scale of heterogeneity’, indicating that at the macroscopic level, variations, say in permeability, may occur at different scales. In fact, this multiple scale heterogeneity is a dominant factor in the subsurface. Because pressure propagates very fast, the effect of this inherent heterogeneity is less noticeable when considering fluid flow. However, its effect on the transfer of the mass of a dissolved chemical species is significant.

In principle, it should be possible to solve a transport problem at the macroscopic level in any heterogeneous domain in which the spatial variations of the permeability and the other relevant coefficients are known. Indeed, in small scale field problems, e.g., in the vicinity of an injection well, or for a small distance downstream of a pollution source, the formation properties (porosity, permeability, dispersivity) may be known (or estimated), and the problem of predicting the concentration distribution of the injected solute, or of the advancing pollution plume, can be solved by making use of the (macroscopic level deterministic) model described in this chapter. However, usually, especially if we are interested in a pollution plume that advances a large distance, sometimes measured in kilometers, 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 known, due to the heterogeneity inherent in such domains. The way we overcome the lack of information about the heterogeneity at the microscopic level (resulting from pore scale heterogeneity) is to use homogenization, or averaging over an REV, as discussed in Sec. 1.3. One may visualize this averaging as a *smoothing operation*. As a consequence of the averaging process, the phenomenon of dispersion was introduced. The same averaging, or smoothing approach, may also be applied to heterogeneities that are encountered at the macroscopic level, to obtain a continuum at the *megascopic level*. Such an averaging volume was referred to as the *representative macroscopic volume* (RMV) (Subs. 1.3.4B). As indicated in (1.3.14), the characteristic size of this volume,  $\ell^*$ , 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 porous medium do-

main. Similar to what happens during microscopic-to-macroscopic smoothing, here, the information about the heterogeneity at the macroscopic level appears at the megascopic level in the form of various coefficients.

Denoting the volume of an RMV by  $\overline{\mathcal{U}}_o$ , and the *macroscopic value* of  $e$  by  $\overline{e}$ , we define the *megascopic value* of  $e$  by:

$$\overline{\overline{e}}(\mathbf{x}, t) \equiv \frac{1}{\overline{\mathcal{U}}_o} \int_{\overline{\mathcal{U}}_o} \overline{e}(\mathbf{x}', t; \mathbf{x}) d\overline{\mathcal{U}}_o(\mathbf{x}'), \quad (7.1.67)$$

where  $\mathbf{x}$  and  $\mathbf{x}'$  denote the centroid of the RMV and of a point (of the porous medium regarded as a continuum) inside it, respectively. With this definition, we may now derive the total flux of a  $\gamma$ -component at the megascopic level, by averaging (7.1.65) over an RMV. For saturated flow, we obtain:

$$\begin{aligned} \overline{\overline{\theta \mathbf{J}^{t\gamma}}} &= \overline{\overline{c^f} \mathbf{q}} + \overline{\overline{\phi (\mathbf{J}^\gamma + \mathbf{J}^{*\gamma})}} \\ &= \overline{\overline{c^f} \overline{\mathbf{q}}} + \overline{\overline{c^f} \hat{\mathbf{q}}} + \overline{\overline{\phi (\mathbf{J}^\gamma + \mathbf{J}^{*\gamma})}} \\ &\approx \overline{\overline{c^f} \overline{\mathbf{q}}} + \overline{\overline{c^f} \hat{\mathbf{q}}}, \end{aligned} \quad (7.1.68)$$

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

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

is the deviation of a macroscopic value at any point within an RMV, from its average over the RMV. We note that the flux on the left-hand side of (7.1.68) (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  $\overline{\overline{c^f} \hat{\mathbf{q}}}$ , which will be referred to as the *macrodispersive flux* of the chemical species. 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 line of (7.1.68) 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 is done for describing transport at the macroscopic level. We usually *assume* that a Fickian-type dispersion law, e.g., (7.1.32), is also valid for describing the macrodispersive flux. A *macrodispersivity*,  $\mathbf{a}_{ijkm}$ , can be defined in the same way as the dispersivity was defined earlier in (7.1.39). Bear (1979), 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 in the form:

$$a_{ijkm} = \frac{\overline{\tilde{K}_{in}\tilde{K}_{j\ell}}}{\overline{K_{kn}}\overline{K_{m\ell}}}\tilde{L}, \quad (7.1.69)$$

where  $K_{ij}$  denotes the  $ij$ -th component of the hydraulic conductivity tensor, and  $\tilde{L}$  is a length that characterizes the inhomogeneity of the aquifer, resulting from stratification. It is a fourth rank tensor, which is analogous to the dispersivity at the macroscopic level (i.e., with  $a_L$  and  $a_T$ , etc.). In an isotropic porous medium, the macrodispersivity reduces to a scalar. Gelhar (1976) and Gelhar *et al.* (1979) analyzed the dependence of macrodispersion on permeability variations. For horizontal flow in an isotropic confined aquifer, they suggested that

$$a_L = \frac{1}{3} \frac{L_1^2 \sigma_{\ln k}^2}{a_T}, \quad (7.1.70)$$

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

Altogether, we may summarize this topic by suggesting that dispersion and macrodispersion are analogous phenomena, in that both are consequences of velocity variations that are due to heterogeneity, but at different scales. Dispersion arises from velocity variations *within* the void space (i.e., at the microscopic level), caused by the presence of the solid surfaces. Macrodispersion is produced by macroscopic velocity variations, caused by variations in the permeability and porosity. In both cases, the flux is the sum 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. In practice, we use exactly the same mathematical model (except that in the case of field scale, we usually neglect the flux due to molecular diffusion), but select the magnitude of the dispersivity according to the scale of heterogeneity.

In laboratory column experiments, the porous medium is more or less homogeneous, say with respect to permeability and porosity. The scale of heterogeneity is that of the size of a grain or a pore. Indeed, the magnitude of longitudinal dispersivity found in numerous column experiments is approximately equal to a pore- or grain-size. However, under field conditions, the scale of heterogeneity, due to variability in permeability and porosity, is much larger. In fact *this scale grows with the size of the domain*. Gelhar *et al.* (1992) compiled a large number of field experiments and presented the observed longitudinal dispersivities,  $a_L$ , as a function of the travel distance,  $L_s$ , as shown in Fig. 7.1.5. It is clear that macrodispersivity is proportional to the size of

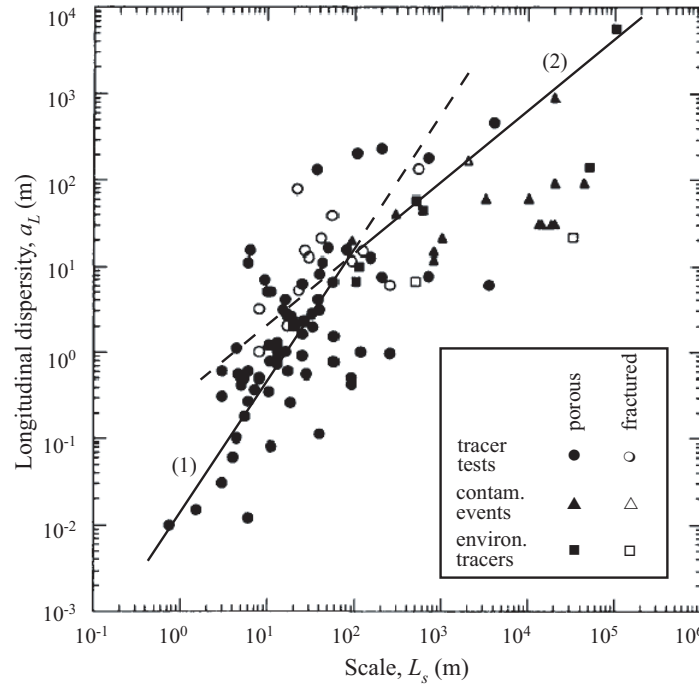


Figure 7.1.5: Longitudinal dispersivity versus plume travel distance for various types of observations and media (Gelhar *et al.*, 1992). Line marked as (1): equation (7.1.71); and (2): equation (7.1.72).

the field, although the data shows a wide range of scatter. Lallemand-Barrés and Peaudecerf (1978) analyzed published values of dispersivity and showed that, on the average, the dispersivity increases with the distance (between a few meters and 10 km), between the source and the point of observation. As a ‘rule of thumb’, they concluded that the dispersivity can be approximated as 1/10 of the distance traveled. This is often referred to as a ‘scale effect’.

Based on the argument of self-similar (fractal) hierarchy of logarithmic hydraulic conductivity, Neuman (1990) suggested a universal scaling law and presented the following equations based on the least square fit of the data:

$$a_L = 0.017 L_s^{1.5}; \quad L_s \leq 100 \text{ m}; \quad (7.1.71)$$

$$a_L = 0.32 L_s^{0.83}; \quad L_s > 100 \text{ m}. \quad (7.1.72)$$

These two empirical formulas are plotted in Fig. 7.1.5. Gelhar *et al.* (1992, 1993), however, cautioned the use of these power laws by pointing out the large scatter in data (2–3 orders of magnitude) in Fig. 7.1.5.

Gelhar and Axness (1983) and Dagan (1984) (see also (7.1.70)) showed that the longitudinal dispersivity is also proportional to the product of the variance of the logarithm of the hydraulic conductivity, and the correlation length scale, i.e.,

$$a_L \sim L_1 \sigma_{\ln k}^2. \quad (7.1.73)$$

This can explain the range of scatter observed in Fig. 7.1.5.

In practice, often, the first estimate of the longitudinal dispersivity, prior to actual calibration, is taken as 1/10 of the size of the *domain of interest*. Thus, for example, for a domain of interest which is 10 m long, we estimate  $a_L = 1$  m. For a domain that is hundreds of meters in size, we estimate  $a_L$  in the range of tens of meters. The horizontal transverse dispersivity is estimated as approximately equal to about 1/10 of the longitudinal one. The vertical transverse dispersivity, in a layered horizontal aquifer, is 1–2 orders of magnitude smaller than the horizontal one (Gelhar *et al.*, 1992). Obviously, these are merely orders of magnitude and may be used as initial or preliminary estimates only. In each particular case, the actual value should be determined by some model calibration procedure.

Apart from the different magnitude of the dispersivity to be employed, the expressions for advective and dispersive fluxes presented in Subs. 7.1.2 and 7.1.5 may be assumed to remain valid when modeling field conditions.

## 7.2 Balance Equation for Single Species

As in the case of fluid flow, the flux equation, (7.1.65), contains two variables: the total flux and the concentration. This means that we need one more equation; this is the mass balance equation for the  $\gamma$ -species. We have not counted the velocity as a variable as we can obtain it by writing and solving the relevant flow model.

We have already introduced the concept of the balance of an extensive quantity in Chap. 5, where we considered the balance of fluid mass. In this section, we are interested in the balance of the mass of a chemical species, or a component dissolved in a fluid phase. We shall introduce this topic through a very simple model. In spite of its simplicity, this model may provide useful insight in practice, especially during the initial stage of an investigation, by indicating whether or not a more sophisticated model is required.

### 7.2.1 Single cell model

As explained in Subs. 5.1.1, a balance is written for an extensive quantity within a *specified spatial domain*, for a *specified period* of time. Let us denote the time interval by  $\Delta t$ , and the volume of the porous medium domain for which the balance is written by  $\mathcal{U}_o$ . A balance of this kind describes the integrated behavior within the domain, usually referred to as a *cell*, or *compartment*, during the balance period. Sometimes, we consider a number of

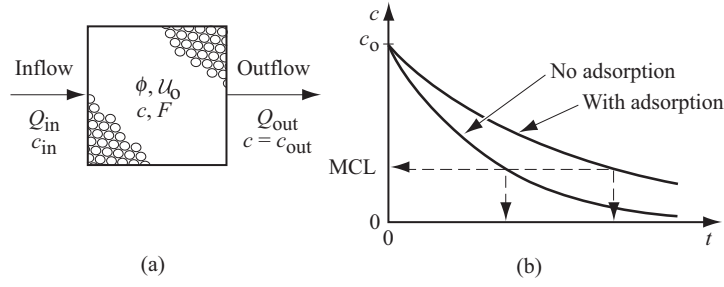


Figure 7.2.1: (a) A single cell model. (b)  $c = c(t)$  in the cell.

adjacent cells, in a one-, two-, or three-dimensional configuration. To obtain the integrated behavior in the cell *at a point in time*, we divide both sides of the balance equation by  $\Delta t$ , and let  $\Delta t$  shrink to zero. When both the finite volume around a point in space and the time interval around a point in time are shrunk to the limiting value of zero, we obtain the description of the behavior at a point in space and in time in the form of a partial differential equation. This is of interest whenever state variables and fluid- and solid-phase properties vary spatially within a domain.

We start by considering a cell (Fig. 7.2.1) of finite volume and a finite time interval. In writing a balance for a cell, it is assumed that all fluid and porous medium properties (e.g., porosity,  $\phi$ , and partitioning coefficient,  $K_d$ ) and all state variables, (e.g., fluid density, component concentration, and fluid pressure) are uniform within  $\mathcal{U}_o$ . This assumption means that the quantity the considered chemical species present in the cell is continuously mixed to form a uniform mixture.

Let us express the verbal statement of balance presented in (5.1.1) in a mathematical form for the mass of a  $\gamma$ -species (concentration  $c$ ) within a fluid phase that occupies the void space at a saturation  $S$ . We assume that the solid matrix is nondeformable, i.e.,  $\partial\phi/\partial t = 0$ , and that the fluid is incompressible, i.e.,  $\partial\rho/\partial p = 0$ .

The quantity of the  $\gamma$ -species within the cell is expressed by  $\phi S \mathcal{U}_o c^\gamma$ , so that the balance of  $\gamma$  within  $\mathcal{U}_o$ , during a time interval  $\Delta t$ , takes the form:

$$(\phi S \mathcal{U}_o c^\gamma)|_{t+\Delta t} - (\phi S \mathcal{U}_o c^\gamma)|_t = \Delta t (Q_{in} c_{in}^\gamma - Q_{out} c^\gamma + f^\gamma \mathcal{U}_o + \phi S \mathcal{U}_o \rho \Gamma^\gamma). \quad (7.2.1)$$

Here,  $c_{in}^\gamma$  is the  $\gamma$ -concentration in the incoming fluid. The total rates of fluid inflow and outflow are given by  $Q_{in}$  and  $Q_{out}$ , respectively. The symbol  $f^\gamma$  denotes the *rate* (= mass per unit time) at which the  $\gamma$ -species moves from the solid and from all other fluid phases into the considered fluid phase across their common microscopic boundaries, per unit volume of porous medium, and  $\Gamma^\gamma$  denotes the *rate* of production of  $\gamma$  within the fluid phase (e.g., by chemical reactions), per unit mass of fluid (of mass density  $\rho$ ).



In order to write the balance for a point in time, we divide (7.2.1) by  $\Delta t$  and let  $\Delta t \rightarrow 0$ , obtaining

$$\lim_{\Delta t \rightarrow 0} \frac{(\phi S \mathcal{U}_o c^\gamma)|_{t+\Delta t} - (\phi S \mathcal{U}_o c^\gamma)|_t}{\Delta t} = Q_{\text{in}} c_{\text{in}}^\gamma - Q_{\text{out}} c^\gamma + f^\gamma \mathcal{U}_o + \phi S \mathcal{U}_o \rho \Gamma^\gamma, \quad (7.2.2)$$

or, according to the definition of a derivative

$$\frac{d}{dt}(\phi S \mathcal{U}_o c^\gamma) = Q_{\text{in}} c_{\text{in}}^\gamma - Q_{\text{out}} c^\gamma + f^\gamma \mathcal{U}_o + \phi S \mathcal{U}_o \rho \Gamma^\gamma. \quad (7.2.3)$$

Dividing this equation by  $\mathcal{U}_o$ , we obtain a balance *per unit volume of porous medium*. Recalling that we have assumed uniformity within the cell, the balance equation that describes the behavior within the cell becomes

$$\frac{d}{dt}(\phi S c^\gamma) = \frac{1}{\mathcal{U}_o} (Q_{\text{in}} c_{\text{in}}^\gamma - Q_{\text{out}} c^\gamma) + f^\gamma + \phi S \rho \Gamma^\gamma. \quad (7.2.4)$$

In a similar way, we can derive a mass balance equation for a  $\gamma$ -species that adsorbs on the solid. We obtain

$$\frac{d}{dt}(\rho_b F^\gamma) = -f^\gamma + \rho_b \Gamma_s^\gamma, \quad (7.2.5)$$

where  $F^\gamma$  denotes the mass of  $\gamma$  *per unit mass of solid*,  $\rho_b (\equiv (1 - \phi)\rho_s)$  denotes the *bulk density of the solid*, and  $\Gamma_s^\gamma$  denotes the *rate of production of  $\gamma$  adsorbed on the solid*, per unit mass of solid.

We shall consider the following four cases:

**CASE A.** Let the fluid phase be a liquid that completely saturates the porous medium domain. Suppose that  $Q_{\text{in}} = Q_{\text{out}}$ , and that the  $\gamma$ -species does not adsorb, decay, or undergo any chemical transformation. Then, (7.2.4) reduces to

$$\frac{dc^\gamma}{dt} = \frac{Q_{\text{in}}}{\phi \mathcal{U}_o} (c_{\text{in}}^\gamma - c^\gamma). \quad (7.2.6)$$

For the conditions,  $c^\gamma = c_o^\gamma$  at  $t = 0$  and  $c_{\text{in}}^\gamma = 0$  for  $t \geq 0$ , the solution of this equation is

$$c^\gamma(t) = c_o^\gamma \exp \left[ - \left( \frac{Q_{\text{in}}}{\phi \mathcal{U}_o} \right) t \right]. \quad (7.2.7)$$

The lower curve in Fig. 7.2.1b presents (7.2.7) in graphical form. The product  $\phi \mathcal{U}_o$  that expresses the volume of void space within  $\mathcal{U}_o$  is usually referred to as ‘one pore volume’. The quotient  $\phi \mathcal{U}_o / Q_{\text{in}}$  gives the time required to flush the fluid through the cell once, assuming complete flushing. We refer to this time interval as *residence time*, because it is the average time that a liquid particle stays in the cell while undergoing continuous, but incomplete flushing. Because of the continuous mixing that we have assumed to take place in the cell, its concentration, as indicated by (7.2.7), is gradually reduced. It

may require the flushing of a number of pore volumes in order to reduce the initial concentration in the cell to a desired level, e.g., down to the MCL (maximum contaminant level), in the case of a contaminant.

**CASE B.** We shall continue under the same assumptions as in Case A, except that the  $\gamma$ -species may adsorb onto the solid under equilibrium conditions, obeying the linear isotherm,  $F^\gamma = K_d c^\gamma$ . A detailed discussion on adsorption under equilibrium conditions is presented in Subs. 7.3.3. The mass of  $\gamma$  in the liquid, per unit volume of porous medium, is given by  $\phi c^\gamma$ , while, e.g. according to the linear isotherm (7.3.66), the mass of  $\gamma$  adsorbed on the solid, per unit volume of porous medium, is given by  $(1 - \phi)\rho_s F^\gamma = \rho_b F^\gamma = \rho_b K_d c^\gamma$ . The total mass of  $\gamma$  per unit volume of porous medium,  $\rho_{\text{pm}}^\gamma$ , is, therefore,

$$\rho_{\text{pm}}^\gamma = \phi c^\gamma + \rho_b K_d c^\gamma = \phi \left( 1 + \frac{\rho_b K_d}{\phi} \right) c^\gamma = \phi R_d c^\gamma, \quad (7.2.8)$$

where

$$R_d \equiv 1 + \frac{\rho_b K_d}{\phi} \geq 1 \quad (7.2.9)$$

is a coefficient that expresses the partitioning of  $\gamma$  within a unit volume of porous medium: for one unit of mass of  $\gamma$  in the liquid, we have  $\rho_b K_d / \phi$  mass units on the solid. For a nonlinear isotherm, say,  $F = K_d (c^\gamma)^n$ , the coefficient  $R_d$  takes the form:

$$R_d = R_d(c^\gamma) = 1 + \frac{\rho_b K_d (c^\gamma)^{n-1}}{\phi}. \quad (7.2.10)$$

For the linear isotherm, the balance equation is

$$\frac{dc^\gamma}{dt} = - \left( \frac{Q_{\text{in}}}{R_d \phi \mathcal{U}_o} \right) c^\gamma, \quad (7.2.11)$$

with its solution

$$c^\gamma(t) = c_o^\gamma \exp \left[ - \left( \frac{Q_{\text{in}}}{R_d \phi \mathcal{U}_o} \right) t \right]. \quad (7.2.12)$$

Note that (1) the same mass balance equation can be obtained by summing (7.2.4) and (7.2.5), since the terms expressing the exchange between the fluid and the solid cancel each other, and (2) the solutions (7.2.7) and (7.2.12) are similar, except for the role played by  $R_d$ .

The upper curve in Fig. 7.2.1b presents (7.2.12) in graphical form. Since  $R_d > 1$  (under the assumption of  $K_d > 0$ ), we note that the time required for reducing the concentration in the cell to a desired level is longer with adsorption than without it. The flushing of the  $\gamma$ -contaminant is slower than that of the host liquid. We say that the movement of the contaminant is *retarded*, relative to the liquid. The coefficient  $R_d$  is, therefore, referred to

as *retardation coefficient* (or *factor*). This coefficient is further discussed in Subs. 7.4.2. We may now define an *effective residence time* equal to the quotient  $R_d\phi\mathcal{U}_o/Q_{\text{in}}$ ; it indicates the average time that the  $\gamma$ -contaminant stays in the cell that undergoes continuous, but incomplete flushing.

**CASE C.** The conditions are similar to those of Case B, except that the contaminant undergoes a first order (e.g., radioactive) decay described by

$$\rho\Gamma^\gamma = -\lambda c^\gamma, \quad \Gamma_s^\gamma = -\lambda F^\gamma, \quad (7.2.13)$$

following from (7.3.53). The balance equation is

$$\frac{dc^\gamma}{dt} = -\left(\frac{Q_{\text{in}}}{R_d\phi\mathcal{U}_o} + \lambda\right)c^\gamma, \quad (7.2.14)$$

with its solution

$$c^\gamma(t) = c_o^\gamma \exp\left[-\left(\frac{Q_{\text{in}}}{R_d\phi\mathcal{U}_o} + \lambda\right)t\right]. \quad (7.2.15)$$

Note that if the liquid occupies only part of the void space, at saturation  $S_\ell$ , assumed to remain constant during the flushing, we must replace  $\phi$  by  $\phi S_\ell$  in (7.2.8) through (7.2.15). The effective residence time is, then,  $S_\ell\phi\mathcal{U}_o R_d/Q_{\text{in}}$ .

**CASE D.** Here, the void space is occupied by a liquid water phase at a constant saturation  $S_w$  and a gas phase at saturation  $S_g$ . The gas phase pressure is assumed to stay at approximately a constant value so that its density does not change appreciably. The  $\gamma$ -contaminant is a volatile one, partitioned between the liquid, the solid, and the gas (at constant pressure). The partitioning of a volatile species between a liquid and a gas, through a common interface, under equilibrium conditions, is assumed to obey Henry's law (presented and discussed in Subs. 7.3.5), written here in the form

$$c_g^\gamma = \mathcal{H}c_w^\gamma. \quad (7.2.16)$$

Inflow and outflow are only of the gaseous phase (as in 'Vapor Extraction'; Subs. 7.10.4). The evaporation and condensation of water is not considered.

The mass of  $\gamma$  per unit volume of porous medium in the liquid ( $w$ ), in the gas ( $g$ ), and on the solid, are now

$$\phi S_w c_w^\gamma, \quad \phi S_g c_g^\gamma, \quad \text{and} \quad \rho_b F^\gamma,$$

respectively. Let us choose  $c_g$  as the unknown variable of the problem. We wish to predict future  $c_g^\gamma$ -concentrations. Obviously, once  $c_g^\gamma(t)$  is known, we can calculate  $c_w^\gamma(t)$ , and  $F^\gamma(t)$ .

Thus, the total mass of  $\gamma$  per unit volume of porous medium can be written as

$$\begin{aligned}
\phi S_g c_g^\gamma + \phi S_w c_w^\gamma + \rho_b F^\gamma &= S_g \phi \left( 1 + \frac{S_w}{S_g \mathcal{H}} + \frac{\rho_b K_d}{S_g \phi \mathcal{H}} \right) c_g^\gamma = S_g \phi R_v c_g^\gamma \\
&= S_w \phi \left( \frac{S_g \mathcal{H}}{S_w} + R_d \right) c_w^\gamma = S_g \phi \left( 1 + \frac{S_w R_d}{S_g \mathcal{H}} \right) c_g^\gamma,
\end{aligned} \tag{7.2.17}$$

where

$$R_d \equiv 1 + \frac{\rho_b K_d}{S_w \phi}, \quad \text{and} \quad R_v \equiv 1 + \frac{S_w}{S_g \mathcal{H}} + \frac{\rho_b K_d}{S_g \phi \mathcal{H}}. \tag{7.2.18}$$

Here,  $R_v$  is another kind of retardation coefficient, this time for the concentration of a volatile species in a gas phase. Without volatilization,  $\mathcal{H} = 0$ ,  $c_g^\gamma = 0$ , and the total mass of the species per unit volume of porous medium is expressed by  $S_w \phi R_d c_w^\gamma$ . The solution, under the same conditions on  $c_g^\gamma(t)$  as those for  $c^\gamma(t)$  in Case B above, is

$$c_g^\gamma(t) = c_{go}^\gamma \exp \left[ - \left( \frac{Q_{in}}{R_v \phi \mathcal{U}_o} \right) t \right], \tag{7.2.19}$$

where we recall that the inflow of the gas has been assumed to be equal to the outflow (that removes the mass of  $\gamma$  from the cell).

The single cell models described in this subsection may be employed to obtain preliminary estimates of clean-up times required in order to reduce concentrations to below permissible levels. In the following subsection, we shall extend our analysis to balance equations that describe transport in porous medium domains visualized as continua that involve spatial variations in material properties, fluxes, and state variables.

### 7.2.2 Fundamental balance equation

Our objective here is to develop the differential balance equation for the mass of a chemical species in a fluid phase that fully or partly occupies the void space. We shall follow the same methodology as used for developing the balance equation for the mass of a fluid phase in both saturated and unsaturated flow.

We consider the case of a  $\gamma$ -species (e.g., a contaminant) in a fluid  $\alpha$ -phase (liquid, or gas) that occupies the entire void space, or part of it, at a fluid content  $\theta_\alpha (= \phi S_\alpha)$  that is allowed to vary in space. Since we are considering here only a single fluid phase, and only a single chemical species, the subscript  $\alpha$  and the superscript  $\gamma$  will be omitted wherever possible.

The starting point may be the microscopic balance equation (5.1.1) for any extensive quantity  $E$ , in which  $E$  is replaced by ‘mass of a  $\gamma$ -species’, and the resulting differential  $E$ -balance equation (5.1.4), at the microscopic level, in which  $e$  is replaced by the concentration  $c \equiv c^\gamma$ .

The macroscopic differential mass balance equation for a component in a fluid phase may be obtained either by writing the microscopic balance

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