Chapter XII

Modelling Solute Transport Using the Double Porous Medium Approach

Andreas JAKOB
Paul Scherrer Institut
Würenlingen and Villigen
CH-5232 Villigen PSI (Switzerland)

XII.1. Introduction

We encounter transport phenomena in every day life: when heating water for coffee, when using electric implements; even the soil-water rising in plants is a transport phenomenon. These flow or transport processes include heat flow, electric current, mass transfer, or more complex processes such as the movement of chemically reactive, viscous and heat-conductive fluids, galvano electric effects, etc. Such processes are governed by laws which will be partially addressed in this chapter. It is evident that a sound theoretical understanding of the principles of these transport processes¹ is essential for those who work in pure or applied physics, physical chemistry, soil physics, meteorology, biology and those dealing with the long-term behaviour of hazardous waste repositories.

The basic physics of transport phenomena is described by non-equilibrium thermodynamics, which is the frame for the macroscopic description of irreversible processes. We confine our discussion to laminar flows and transport processes only; turbulent flow is not considered in the following. The treatment of transport phenomena as such is part of macroscopic physics and is related to other macroscopic disciplines like fluid dynamics and electrodynamics. The media in which transport phenomena occur are regarded as

¹ Words written in italics are explained in a glossary at the end of this chapter.
Modelling Solute Transport Using the Double Porous Medium Approach

continua, and processes on a microscopic scale are not considered. The advantage of using macroscopic equations is obvious. A microscopic description would typically require a system of about $10^{23}$ coupled differential equations (the set of equations of motion) to be solved with the pertinent number of parameters. It would be a hopeless task to try to solve such a system of equations in a reasonable time span. Instead one must replace the microscopic quantities by the macroscopic continuum quantities by using a carefully chosen REV (Representative Elementary Volume). This procedure is based on the idea that there exists a scale for the porous medium below which the microscopic equations have to be allied, and above which the geometry of the phases can be averaged. By doing this, the porous medium is replaced by a fictitious continuum at the macroscopic scale. The unknown details on the microscopic scale are replaced by a few averaged parameter values at the macroscopic scale. These averaged parameter values can be measured in suitable experiments and used in macroscopic equations to arrive at a predictive model.

The first objective of this chapter is to give a short and rather qualitative overview of the large domain of non-equilibrium thermodynamics. Our aim is to present some transport phenomena which can be described by similar mathematical equations. However, it is not our purpose to present a formal description of all the effects and to discuss their consequences in detail. This can be found in a textbook. Our approach is not a sophisticated one; after the introduction, we will restrict the transport phenomena to those which are described by Fick’s law - i.e., by mass transport due to a concentration gradient.

Using a simple continuum model\(^2\) for transport of a solute in porous media we will highlight some aspects of the concept of Fickian dispersion but also mention its principal limitations. One such limitation is the still-open question of the scaling-up of the values for the dispersivity tensor obtained from small-scale experiments. We will see that the Peclet number (cf. p.535) is of little importance for this problem contrary to the Reynolds number in fluid dynamics (cf. footnote on page 536). Other limitations are due to the effects of a fracture network or channelling.

For the solute/rock interactions, we will restrict ourselves to sorption processes which can be formulated with the help of an isotherm formalism and we will neglect more complicated processes such as precipitation and dissolution, redox-reactions, etc.

As an additional important transport mechanism we will discuss the influence of unlimited and limited matrix diffusion in the frame of the double porosity medium concept. When molecular diffusion of a solute into the adjacent rock matrix beneath a fracture is sufficiently fast, the effect of matrix diffusion can be estimated with high precision using the effective surface sorption approximation. Its efficiency and simplicity makes this approximation an appreciated and fast “tool” for a modeller.

Physics describes reality with the help of models, and models are abstractions, i.e., descriptions which consider only certain aspects of nature. Moreover, a given physi-

\(^2\) At this point we would like to refer to the article by T. Karapiperis in this book (Chapter XI), wherein coupled transport and chemical reactions are modelled by means of a cellular automaton in discrete space and time. This approach is especially appropriate for the class of problems lying in the intermediate region between the macroscopic and microscopic length scales ($\approx 1$ cm and $\approx 1$ Å, respectively), such as, e.g., the evolution of porosity as a result of solute-mineral reactions.
Classification of transport phenomena

cal phenomenon can be described by different models using different assumptions and approximations and with different degrees of sophistication according to the individual requirements. Both the complexity and the accuracy of models are important issues. In order to decide on the adequacy and accuracy of models, they have to be compared with experiments, and differences have to be ascertained. With this procedure one tries to quantify the quality of a given model, e.g. by determining the minimum value of the $\chi^2$-merit function by fitting experimental data with a suitable model. A real test for a model, however, is its predictive capacity for experimental data or even of new phenomena. Therefore, in the last section, we will discuss experimental data from various experiments and compare them with different continuum concepts. By starting with a simple model (e.g. the “equivalent porous medium model”), comparing the model with experimental data, ascertaining the differences quantitatively, refining the concept (e.g., using the “double porosity medium model”) and arriving at a deeper knowledge, we will demonstrate the iterative procedure of modelling and also point out open questions and unresolved problems.

XII.2. Classification of transport phenomena

There are different ways to organise a discussion of transport phenomena. A simple classification based on the entity being transported results in the following scheme:

- transport of momentum [Ns],
- transport of energy (heat) [Nm],
- transport of electrical charge [$C$],
- transport of mass [kg].

It is a natural tendency among closed physical systems out of equilibrium to approach a state of equilibrium by transport of an entity. These are the spatial inhomogeneities (a difference) of a quantity which start the transport of another (extensive) quantity. Transport - a flow (or current or transfer) - of a quantity occurs due to a “driving force”. Examples of driving forces are, e.g., a spatial difference in the velocity field, in temperature, in the concentration or, in a generalised thermodynamic potential. If a given (thermodynamic) state is not too far away from equilibrium, it is reasonable to assume a linear relationship between flux$^4$ and driving force. This means that in a first approximation, the flux is a linear function of the driving force$^5$. This phenomenological relationship

$^3$ The transported quantity is extensive, whereas the quantity causing transport is intensive.

$^4$ By the term “flux” we mean “rate of flow per unit area” (e.g., [Current density] = $\frac{C}{m^2s}$, or [Diffusive flux] = $\frac{mole}{m^2s}$).

$^5$ Certain irreversible processes should be described by non-linear relations. However, the adequate description of such processes is beyond the scope of this chapter and will not be considered here. Thus, “ordinary” transport phenomena, such as heat conduction and electric current are approximated by linear relations, even if the experimental conditions are rather extreme, whereas chemical reactions must be described by non-linear relations.
between the gradient $\vec{\nabla}$ of a quantity $\varphi$ - the driving force - and the flux $\vec{j}$ is of the form:

$$\vec{j} = -C \cdot \vec{\nabla} \varphi$$  \hspace{1cm} (XII.1)

with the transport coefficient $C$. For example, a velocity gradient causes a momentum flux; a temperature gradient a heat flux; or a gradient of the electrical potential the transport of charge, *etc.* But things are even more complicated. It is a well-known fact that electrically charged particles (*e.g.*, ions) also carry mass. Hence, an electric current, due to the gradient of the electrical potential, is automatically coupled with mass transfer, a process established in science and technology under the name of electrophoresis or electro-osmosis. In addition, a concentration gradient causes mass transport, a process which is accompanied by a viscous flow, known as chemical osmosis. Indeed, experiments show that transport of an entity may be caused by different gradients, and therefore Eq. (XII.1) should actually be expressed as a sum of all possible gradients. Taking into account all combinations of gradients and fluxes, we end up with a matrix (the scheme) of the coupled transport processes.

There are practical reasons why volume/fluid flux rather than momentum flux is considered in Table XII.1. Hence, the hydraulic head gradient instead of the velocity gradient enters the scheme. (The word “law” for the effects in the diagonal of the matrix of coupled processes is traditional and also used here.)

The quantities $C$ in Eq. (XII.1) are phenomenological (transport) or kinetic coefficients and have to be determined experimentally. These coefficients are functions of the medium, composition, temperature, pressure, *etc.* More precisely, the transport coefficients of Table XII.1 are second rank tensors, and it is assumed that they are dependent on the local properties of a solid or mobile phase and possibly also on the local value of $\varphi$, but not on $\vec{\nabla} \varphi$. As examples, some of the (diagonal) coefficients are listed below:

- the hydraulic conductivity $K$ [m/s] in the case of volume/fluid flux,
- the thermal conductivity $\kappa$ [W · m$^{-1}$ · (°K)$^{-1}$] for transport of energy/heat,

---

Table XII.1: Table of coupled processes.

<table>
<thead>
<tr>
<th>Flux</th>
<th>Driving force (gradient of)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydraulic head</td>
</tr>
<tr>
<td>Volume/Fluid</td>
<td>Darcy's law</td>
</tr>
<tr>
<td>Energy/Heat</td>
<td>Thermal filtration</td>
</tr>
<tr>
<td>Electric charge</td>
<td>Rouss effect</td>
</tr>
<tr>
<td>Mass</td>
<td>Ultrafiltration</td>
</tr>
</tbody>
</table>

---

6 In most cases $\varphi$ is a *scalar* and $\vec{j}$ a *vector*. If, in addition, the medium is *isotropic*, $\vec{j}$ points in the direction of the most rapid decrease of $\varphi(\vec{r})$, which is the reason for the minus sign in Eq. (XII.1). (However, if $\varphi$ is the velocity $\vec{v}$, then $\vec{\nabla} \varphi$ and $\vec{j}$ are *tensors.*
Mass transport due to a concentration gradient

- the electrical conductivity $\sigma \ [\Omega \cdot m^{-1}]$ for transport of electrical charge,
- the diffusivity $D \ [m^2/s]$ for transport of mass.

For a homogeneous material, $C$ can only depend on position through any dependence of $\varphi$. For isotropic materials, $C$ must have a form which is independent of all spatial directions; hence all sets of orthogonal axes must be principal axes of the coefficient matrix $C$ which is only possible when $C_{ij} = C_{ij} \delta_{ij}$.

As mentioned before, to consider each process and its effect in the matrix of coupled processes (Table XII.1) in detail would be beyond the scope of this chapter. If additional information on particular processes are requested, more details can be obtained from the relevant literature [59LAN/LIF, 60BIR/STE, 86MAR3, 88BRO/HER, 89DAG, 91BEA/BAC, 94BAT].

XII.3. Mass transport due to a concentration gradient

Following these general remarks on transport phenomena we now focus on mass transport as a result of a concentration gradient and we will discuss in more detail some mechanisms which can have a strong influence on mass transport, such as dispersion, sorption, matrix diffusion, etc. For the following we assume that transport of a dissolved substance takes place in a (fractured) porous medium.

Structural geological studies of bore cores give information about the mineral composition, the heterogeneities of the rock, and on the degree of anisotropy and persistency of flow paths. Such investigations also allow assumptions to be made about the porosity and the maximum penetration depth for matrix diffusion. When viewed from the local scale, it seems that geological systems are too complex - even for a description using rather sophisticated models. This is because complicated flow patterns can be recognised which may be associated with grain boundaries of minerals and pore spaces; other flow paths are simple cracks with or without mineral infill. For illustration, we have included some pictures where individual macroscopic features are magnified and disintegrated into micro-structures (see Figure XII.1). This gives an impression of the variability of flow paths and patterns as they appear in a drillcore from granitic rock.

XII.3.1. Fickian dispersion

In a uniform fluid flow field of a single phase, a spherical domain contaminated by a tracer would progress without any spreading. However, slow mixing will occur due to Brownian motion of the particles, i.e. by molecular diffusion. Therefore, the shape of such a traced domain will remain spherical, and the whole domain will increase but with an average

---

7 In 1931 Hartley [31HAR] showed that it is the gradient of the chemical potential rather than the gradient of the concentration which pushes the diffusion process. For our purposes the concentration of a dissolved species will be assumed to be low, so that the gradient of the thermodynamic activity of the dissolved species can be well approximated by the gradient of its concentration. In such a case a concentration gradient can be assumed for the driving force for mass transfer.
Figure XII.1: Sections through a drillcore of granite from the Grimsel underground laboratory (Switzerland). There is a relation between macroscopic deformation features (cleavage trajectories stippled, fault gauges black in the sketch) and the microscopic distribution of flow paths in the micrographs (reprinted with permission from [91BOS/MAZ]).
Mass transport due to a concentration gradient

concentration decreasing with time. Normally, media in which transport takes place are heterogeneous - they are “disordered” on a microscopic scale (e.g., porous media) - and show an additional mixing which is often larger by orders of magnitude than the spreading due to pure molecular diffusion. Such additional spreading of an initially narrow tracer pulse is due to mechanical dispersion. This mechanism is part of the hydrodynamic dispersion, \( D \), which is the sum of the coefficient for mechanical dispersion \( D_{\text{mech}} \) [m\(^2\)/s] and that for the molecular diffusion \( D_{\text{diff}} \) [m\(^2\)/s]:

\[
D = D_{\text{mech}} + D_{\text{diff}} .
\] (XII.2)

With the term mechanical dispersion we denote the drift of tracer particles in a liquid due to microscopic variations of the fluid flow field. Friction of fluid particles on surfaces of the solid phase reduce irreversibly the velocity of these particles. The size and the orientation of micropores have a statistical distribution, therefore, also changing the direction of flowing particles and, at the same time, causing spreading of a substance at right angles to the main flow direction. Dispersive effects are regarded separately from convection, but this is rather arbitrary because averaging over a domain of a porous medium yields a macroscopic dispersive tracer flux in addition to an averaged macroscopic advective tracer flux. The mechanical dispersion is the result of a real and highly complex - and in principle unknown - velocity field on the microscopic scale. Variations in the velocity field mainly cause solute dispersion. It would therefore be completely inadequate to take into account only convection and molecular diffusion as mixing phenomena. For the mathematical treatment of mechanical dispersion, it is very common to assume an expression analogous to that for molecular diffusion - hence, a formula which is also of the Fickian type:

\[
\vec{j}_{\text{mech}} = -\varepsilon D_{\text{mech}} \cdot \vec{\nabla} C .
\] (XII.3)

In this equation \( \vec{j}_{\text{mech}} \) means the (mechanical) dispersive flux in a porous medium (with porosity \( \varepsilon \)) which is mass per unit area of porous medium and unit time of a migrating species. We can see that the expression for the Fickian dispersion may not be appropriate. Eq. (XII.3) implies that \( D_{\text{mech}} \) is a property of matter as is the diffusivity. However, as mentioned above, dispersion is a consequence of a velocity distribution and hence cannot be a property of matter only. It is dependent on the structure of the inhomogeneities of the solid phase which causes the velocity distribution and the fluid flow field.

The most simple geometry for modelling transport of a solute is that of a porous medium assumed to be macroscopically homogeneous and isotropic. For the following considerations we will use Cartesian co-ordinates and we will put its origin so that the \( z \)-axis coincides with the direction of the averaged pore water velocity - \( \langle \vec{v} \rangle \). In a concept with such a simple underlying geometry, the transport coefficients are constant in space and time, and the dispersion tensor is diagonal. Moreover, in such a case the tensor \( D_{\text{mech}} \) is a function of two scalar quantities only and \( D_{\text{diff}} \) is also a scalar quantity, representing the pore diffusivity:
\[
D = (D_{ij})
\]
\[
= \begin{pmatrix}
D_T + D_{\text{diff}} & 0 & 0 \\
0 & D_T + D_{\text{diff}} & 0 \\
0 & 0 & D_L + D_{\text{diff}}
\end{pmatrix}
\]
\[
= \begin{pmatrix}
a_T < |\vec{v}| > + D_{\text{diff}} & 0 & 0 \\
0 & a_T < |\vec{v}| > + D_{\text{diff}} & 0 \\
0 & 0 & a_L < |\vec{v}| > + D_{\text{diff}}
\end{pmatrix}.
\]

\(D_L = a_L < |\vec{v}| >\) is called the coefficient for the longitudinal dispersion, whereas \(D_T = a_T < |\vec{v}| >\) is the coefficient for the transverse dispersion, both being macroscopic quantities and having the dimension \([\text{m}^2/\text{s}]\). The tensor \(D\) is anisotropic even for isotropic media, because the mixing is larger in the direction of the velocity vector than in transverse directions. Therefore Eq. (XII.4) is only valid for uniform flow; otherwise the principal axes (being linked to the mobile and not to the solid phase) for \(D\) would vary over the flow domain.

The mass balance equation governing the transport of a non-reactive (non-sorbing) and non-decaying solute by a fluid with constant density and viscosity through a porous medium is given by (note: the porosity \(\varepsilon\) cancels out if it is constant):

\[
\frac{\partial C}{\partial t} = -\text{div} \vec{j}_{\text{conv}} - \text{div} \vec{j}_{\text{disp}} = -\nabla \cdot (\vec{v} C) + \nabla \cdot (D \cdot \nabla C).
\]

This expression is called the transport equation for convection (advection\(^8\)) and dispersion and is, in general, three-dimensional. Advection/convection describes the mean transport rate of a solute and hydrodynamic dispersion explains the variation of the mean. Due to lack of data, one may have to use a simplified geometry for the transport. The equation is often reduced to two or even one dimension, but this restriction should be justified on the basis of plume observations in the laboratory or in field experiments.

Let us now briefly discuss the one dimensional case, neglecting molecular diffusion. Flow takes place in the \(z\)-direction. Eq. (XII.5) is then reduced to:

\[
\frac{\partial C}{\partial t} = a_L < |\vec{v}| > \frac{\partial^2 C}{\partial z^2} - < |\vec{v}| > \frac{\partial C}{\partial z}.
\]

This equation has been extensively used to describe the transient distribution of solute concentrations. Its popularity is based on the fact that it describes successfully a variety of contaminant transport observations and also that an analytical solution can be obtained for simple initial and boundary conditions.

\(^8\) We use convection and advection as synonyms.
Mass transport due to a concentration gradient

In our example, at \( t = 0 \) a short tracer pulse with release time \( T \) (\( T \ll t \), where \( t \) is the time of interest) is injected at concentration \( C_0 \) [mol/m\(^3\)] into a semi-infinite medium (\( 0 \leq z \leq +\infty \)) which is initially free of solute: hence \( C(z,0) = 0 \), \( \forall z \). We require as a boundary condition downstream at infinity (\( z \to +\infty \)) that the concentration should vanish for all times. An analytical solution can be obtained with the help of Laplace transforms:

\[
C(z,t) = \frac{\Delta m}{\varepsilon F \sqrt{4\pi a_L}} \cdot \exp \left( -\frac{(z-|\vec{v}| t)^2}{4a_L < |\vec{v}| > t} \right),
\]  
(XII.7)

for \( t \gg \frac{a_L}{<|\vec{v}|>} \)

where \( \Delta m = \varepsilon F < |\vec{v}| > TC_0 \) [mol] and \( F \) [m\(^2\)] is the cross-sectional area of the flow. The spatial form of the solution (XII.7) is a symmetric Gaussian curve with mean value \( <z> = <|\vec{v}|> t \), the transport distance due to convection only, and the standard deviation

\[
\sigma_{z,t} = \sqrt{2a_L < |\vec{v}| > t} = \sqrt{2a_L < z>}.
\]  
(XII.8)

\( \sigma \) [m] characterises the spreading due to mechanical dispersion and is proportional to the square root of the travelling length \( <z> \), but not to velocity. For a fixed observation point along the migration pathway at \( <z> = L \), we obtain an asymmetric curve

\[
C(L,t) = \frac{\Delta m}{\varepsilon F < |\vec{v}| > \sqrt{4\pi a_L < |\vec{v}|>}} \cdot \exp \left( -\frac{(t-\frac{L}{<|\vec{v}|>})^2}{4a_L < |\vec{v}|> \frac{L}{<|\vec{v}|>}} \right).
\]  
(XII.9)

From this equation we determine the time when the peak maximum concentration passes location \( L \):

\[
t_{\text{max}} = \frac{L}{<|\vec{v}|>} \left[ \sqrt{1 + \left(\frac{a_L}{L}\right)^2} - \frac{a_L}{L} \right] \approx \frac{L}{<|\vec{v}|>} \left(1 - \frac{a_L}{L}\right).
\]  
(XII.10)

Here we made use of the condition \( a_L \ll L \) so that powers in \( a_L/L \) higher than the linear term can be neglected. If we remember that \( t_{\text{conv}} = L/ <|\vec{v}|> \) holds, we can rewrite Eq. (XII.10):

\[
t_{\text{max}} = t_{\text{conv}} \left(1 - \frac{a_L}{L}\right) < t_{\text{conv}}.
\]  
(XII.11)

Hence, due to mechanical dispersion, the arrival time of the peak maximum at distances \( L > a_L \) is shifted by the term \( a_L/L \) to shorter times. For the maximum peak height we get at the observation point \( z = L \):

\[
C_{\text{max}}(L,t) = \frac{\Delta m}{\varepsilon F \sqrt{4\pi a_L L}} \left(1 + \frac{a_L}{4L}\right) \approx \frac{\Delta m}{\varepsilon F \sqrt{4\pi a_L L}}.
\]  
(XII.12)

---

This is a necessary condition for using a macroscopic continuum approach for modelling transport of a solute in a porous medium.
Modelling Solute Transport Using the Double Porous Medium Approach

Figure XII.2: Spreading and shape of the peak due to mechanical dispersion for a short tracer pulse with initial release time $T$. The travelling time for the tracer pulse due to convection only is $t_{\text{conv}} = \frac{z}{\|\vec{v}\|}$. The left sketch outlines the spatial tracer concentration profile for a fixed time $t$. For short migration distances, the tracer distribution is narrow and high; for larger distances, it decreases and becomes wider. According to Eq. (XII.7) the distribution is Gaussian and, hence, has a symmetric shape. $2\sigma$ is defined by the two points where the curve has its maximum slope. The relative height of these points (equivalent with the two points of inflection) is $\exp(-1/2)$. The right sketch illustrates the temporal tracer concentration distribution at a fixed location. Due to the time dependence of $\sigma$ the shape of the curve is asymmetric and the peak position is slightly earlier than the convection time $t_{\text{conv}}$.

From this expression we easily see that, due to Fickian dispersion, the peak height is:

- proportional to the total released mass $\Delta m$,
- inversely proportional to the porosity $\varepsilon$ and the flow area $F$,
- inversely proportional to the square root of the travel distance $L$ of the solute and, finally,
- inversely proportional to the square root of the (longitudinal) dispersivity $a_L$.

The most important results of this brief discussion are depicted for illustration purposes in Figure XII.2.

Let us briefly address the boundary condition problem. In our example we have chosen a concentration boundary condition upstream which, in the model, causes a mass transfer
Mass transport due to a concentration gradient

due to dispersion in addition to the advective mass transfer across the boundary. For a short tracer pulse with release time $T$, the total mass released $\Delta m$ is composed of the advective and dispersive parts according to

$$\Delta m = \Delta m_{\text{adv}} + \Delta m_{\text{disp}},$$

(XII.13)

where

$$\Delta m_{\text{adv}} = \varepsilon FC_0 < |\vec{v}| > T,$$

(XII.14)

and

$$\Delta m_{\text{disp}} \approx \frac{2}{\sqrt{\pi}} \varepsilon FC_0 \sqrt{a_L} < |\vec{v}| > T \propto \sqrt{T}; \text{ for } T \ll \frac{a_L}{< |\vec{v}| >}.$$ (XII.15)

As $T$ approaches zero, the solute release is purely dispersive, caused by the large concentration gradient which strongly dominates advection. However, this is an effect of the advection/dispersion model only. If the release time becomes sufficiently large, corresponding to a constant concentration input with actual duration $\tilde{T}$, the additional released mass due to dispersion becomes constant and is given by

$$\lim_{T \to \infty} \Delta m_{\text{disp}} = \varepsilon F C_0 a_L.$$ (XII.16)

About 95% of the asymptotic value of $\Delta m_{\text{disp}}$ will have entered the migration zone when the advective transport distance is

$$< |\vec{v}| > \tilde{T} = < z > \geq 8 a_L.$$ (XII.17)

This means that for larger distances the influence of the upstream concentration boundary condition has worn off. Eqs. (XII.16) and (XII.17) show that the dispersive mass transfer across the upstream boundary is negligible for a concentration boundary condition if the release time $\tilde{T}$ allows a sufficiently large advective transport distance. Because only linear mass balance relations are considered, a concentration pulse at the observation time $t = \tilde{T}$ with release time $T$ can be described as the linear superposition (difference) of two step functions with release time $\tilde{T}$ and $(\tilde{T} - T)$, respectively. In this case the total dispersive mass transfer across the upstream boundary sums up exactly to zero giving rise to the relation $\Delta m = \Delta m_{\text{adv}}$ in Eq. (XII.7).

It is important to investigate the conditions under which dispersion cannot be taken into account by the simple convection-dispersion equation.

For very slow convection the spreading due to mechanical dispersion may be negligible compared to the effect of molecular diffusion. However, when the velocity is so large that turbulence occurs, Darcy’s law is no longer applicable. To estimate the effect of molecular diffusion, a dimensionless quantity - the Peclet number - is defined

$$Pe = \frac{< |\vec{v}| > l}{D_{\text{diff}}}.$$ (XII.18)
where \( l \) is a characteristic length of the porous medium (e.g., the pore size) and \( D_{\text{diff}} \) is the molecular diffusion coefficient. The Peclet number is a measure of the competition between convection and molecular diffusion:

- If \( Pe < 0.3 \): Convection is so slow that dispersive effects are dominated by molecular diffusion. Hydrodynamic dispersion therefore is practically isotropic, meaning that a spherical domain of solute will remain spherical, but with increased size for increased time.
- For \( 0.3 < Pe < 5 \): Both processes are about equally important.
- For \( 5 < Pe < 300 \): Convection becomes more and more important and induces increased mechanical dispersion. However, molecular diffusion cannot be neglected.
- For \( 300 < Pe < 10^5 \): The regime of pure mechanical dispersion is reached; molecular diffusion is - for all practical purposes - negligible.
- If \( Pe > 10^5 \): The flow is highly turbulent, and, in addition to the Peclet number, the Reynolds number\(^{10} \) should also be taken into account.

If molecular diffusion can be neglected an alternative Peclet number may be defined as

\[
Pe = \frac{<|\vec{v}|> l}{D_{\text{mech}}}
\]  

This is the transport Peclet number, which is a measure of the competition between convection and mechanical dispersion. The smaller the (transport) Peclet number, the greater the (mechanical) dispersive contribution. In the one-dimensional case, where transverse dispersion is judged to be of little importance, Eq. (XII.19) is reduced to \( Pe = l/\alpha_L \) where \( l \) is considered as the observation distance. Empirically the transport Peclet number has to be greater than about 5, otherwise the microscopic quantities cannot be replaced by macroscopic continuum quantities such as \( D_{\text{mech}} \), and the continuum transport Eq. (XII.5) is no longer appropriate.

The applicability of the simple convection-dispersion equation for describing solute transport in heterogeneous porous media has been thoroughly investigated.

For experiments in more or less homogeneous laboratory columns it was found that the convection-dispersion equation reproduces the experimental data quite well using values for the dispersivity in the order of mm up to cm.

\(^{10}\) Every flow of a viscous liquid which is not frictionless can be characterised by a dimensionless number, the Reynolds number \( Re = \frac{\mu l}{\rho \nu} \), where \( \nu \) is the mean velocity, \( l \) is the hydraulic diameter of the flow domain and \( \mu/\rho \) is the kinematic viscosity. The Reynolds number is given by the ratio of the inertial forces and friction forces; for large \( Re \) the inertial forces are dominant and flow is turbulent, and for small values of \( Re \) flow is laminar. Large/small only makes sense with regard to a reference point, e.g., \( Re_{\text{crit}} \) where laminar flow turns towards turbulent flow. Typical values for \( Re_{\text{crit}} \) are of the size 1000 ... 10000 depending on the roughness of the bounding walls and on the upstream boundary condition. Flow fields in the geosphere are characterised by Reynolds numbers which are orders of magnitude smaller than the critical value; hence, such flow fields can be considered as laminar.
However, for heterogeneous experiments, especially for the case of a stratified porous medium with flow strictly parallel to the stratification, it was shown [80MAT/MAR] that the solute transport cannot be described adequately by the convection-dispersion equation, even when considering large transport times. However, for flow not strictly parallel to the bedding, this theoretical study has shown that Fickian dispersion will occur asymptotically for large transport times.

XII.3.2. Scale dependent dispersivity

Experimental as well as theoretical investigations clearly indicate that dispersivities determined on a field-scale are typically several orders of magnitude larger than values obtained on the laboratory-scale using the same material. Such a scale dependence of the dispersivity is documented, e.g., in [77OAK/EDW, 81PIC/GRI, 92GEL/WEL] and is illustrated by Figure XII.3.

The variation of the dispersivity reflects the influence of differing degrees of the spatial heterogeneities of a medium and, hence, also in local heterogeneities in the hydraulic conductivity. In field experiments, the (longitudinal) dispersivity is of the order of some
meters up to several hundred meters, or even kilometres, depending on the size of the heterogeneities. By using the Peclet number, it is not possible to rescale the results from one type of experiment to another with the help of a similarity law for the real physical systems. Consequently, laboratory measurements of dispersion cannot be used for the extrapolation to large scale experiments. This scaling problem may severely limit the predictive capability of models being calibrated on experiments on the laboratory scale.

Knowledge of transverse dispersion is much less profound than that of longitudinal dispersion. Data indicate that values for transverse dispersion are typically an order of magnitude smaller and can therefore be estimated as a few tenths of the value for $a_L$.

**XII.3.3. The problem of local averaging**

So far we have used a simple formalism for transport of a solute in a porous medium. For illustration purposes we may think in terms of a column experiment with sand as the solid material. A necessary condition for the use of the continuum approach is, as previously outlined, that a REV can be determined which is much smaller than the domain of interest (the length of the column in our example) and larger than the scale of the microscopic heterogeneities (the size of the pores or the size of the grains). Hence, the REV is large enough to encompass all geometrical heterogeneities. At this point the question arises whether the continuum approach is also applicable to fractured porous rock. We define fractured porous rock as a porous medium with void geometry composed by the pore spaces and also by a network of more or less open fractures. Modelling the solute flow in fractured porous rock is largely a problem of defining the geometry of all the fractures. In reality not all systems of fractures constitute a network. Often the fracture density (the number of fractures per unit volume of porous medium) is too low and/or the extent of the fractures (trace length) is too small to constitute a fracture network. Therefore, measurements of the hydraulic conductivity performed tend to be erratic and very sensitive to the volume of fractured porous rock. Such variations of the hydraulic conductivity in a fractured porous medium cause a nonuniform velocity field, whereas the variations in the velocity - as mentioned earlier - mainly cause mixing due to mechanical dispersion. In such a case, a REV can hardly be defined, because its volume may be even larger than the volume of interest, and a formalism based on a continuum approach cannot be developed. In order to describe a transient solute distribution for a system of sparsely connected fractures we would require information on every individual fracture, but this can never be achieved. However, if information on geometrical quantities such as orientation, aperture, etc. can be obtained as statistical values, a statistical description of the solute behaviour can be achieved. If the number of individual fractures is large (ten thousands or even more), as when considering solute transport over larger distances, only statistical distributions for individual parameters can be derived and no local averaging can be performed over a REV.

One approach is to treat the fractured porous medium as an equivalent porous medium, which is appropriate when the individual fractures are densely interconnected and fluid
flow through large regions is considered. In this way, the domain of fractured porous rock can be characterised by a conductivity tensor, and flow and transport can be treated as in a porous medium.

An alternative approach would be the treatment of flow and transport through a number of discrete and interconnected fractures. In the first approach, we consider mixing phenomena like dispersion to be of the Fickian type, hence as spatially invariant, while in the second approach dispersion is strongly non-Fickian. Because a fluid always flows along the least resistive flowpath, a fraction of the solute may be transported in a few preferential flow paths much faster than with the mean transport time. Moreover, the hydraulics and transport properties of such channels may be completely different from those averaging over the whole domain of interest. Further information concerning these problems can be found in [93BEA/TSA].

XII.3.4. Sorption equations used in transport modelling

The geosphere is an exceedingly complex system; not only is it composed of solid, liquid and often gaseous phases, but each of these phases may include reacting inorganic, and organic, components. This strongly heterogeneous character of the geosphere determines and influences the physical and chemical behaviour of the system, and has a direct and strong impact on solute transport. Understanding the physical and chemical transformation of the solute is one of the key problems for modelling the rock-solute complex. Typical phenomena involved in the physical and chemical transformation of solutes are various forms of sorption processes, precipitation, dissolution, oxidation-reduction reactions, volatilisation, maybe biodegradation in the presence of micro-organisms, etc. Given such a high degree of complexity of a solute-rock system, a comprehensive, complete and accurate description with predictive capabilities can never be reached. Nevertheless, in the past major efforts have been made to understand some of these processes and mechanisms, and many models have been developed to describe experimental data adequately and to deduce new information from them.

Some processes, such as volatilisation, irreversible\textsuperscript{11} precipitation or dissolution could roughly be taken into account by the net source/sink terms in the transport equations. Other processes are much more complicated, as described in other chapters in this book\textsuperscript{12}.

Let us now turn our attention towards the description of sorption processes. The term sorption in general refers to the distribution of a solute between an immobile phase and a solution. Examples are physical sorption, chemisorption, \textit{e.g.} surface complexation, ion exchange, isotopic exchange; or ion exclusion, molecular filtration, mineralisation, \textit{etc}. Hence, the term sorption includes a broad variety of physical-chemical processes. Physical adsorption, for example, is a process where solute adheres to the surface of the solid phase.

\textsuperscript{11} Whether a process is considered reversible or irreversible (or: instantaneous or non-instantaneous = kinetics) depends on the timescale involved.

\textsuperscript{12} For a more comprehensive overview on the theoretical framework concerning the chemical transformation and immobilisation of solutes onto surfaces at the solid/liquid interface of geological media, the reader is referred to the chapter by S.A. Banwart in this book (Chapter VII).
The bonding is caused by Van-der-Waals forces and is weaker than when sorption occurs through covalent or ionic bonding as in chemisorption/surface complexation. The capacity to form surface complexes depends on the species dissolved, the pH of the solution, the composition of the water, the minerals of the solid phase present, etc. Anions, as well as cations, may form surface complexes. Ion exchange is a process by which charged particles of the solute replace ions on the surface or within the structure of the solid phase. If the process involves isotopes of the same element, the process is called isotopic exchange. Processes such as ion exclusion and molecular filtration are phenomena associated with solute flow; they do not represent a direct uptake of solute species onto the solid phase as the processes mentioned before. For both processes the mobility of the solute species is restricted by either constrictions along the flow pathway, as in the case of molecular filtration, or by surface charges resulting in a repulsion of similarly charged ions as in the case of ion exclusion. It is conceivable that positively charged solute particles (cations) may reduce the influence of a negatively charged surface resulting in weaker repulsion of migrating ions, less sorption and, hence, less retardation. The term mineralisation describes a direct uptake of ions by the solid phase and includes also precipitation of solids.

The nature of all the processes mentioned leads to retardation of migrating solute species. However, since it is often very difficult to quantify these reactions or even to estimate the relative importance of different sorption processes, simplifications are normally employed. Nevertheless, some characteristics of the sorption mechanisms can be recognised. Most experiments show that the capacity for sorption of a solid phase for a dissolved species tends to increase with increased concentration of the dissolved species (but there are examples where this is not the case).

From a thermodynamic point of view, sorption processes can be divided into reversible and irreversible processes depending on the time scale involved. Furthermore, sorption reactions may be slow or they can rapidly reach an equilibrium state with no further concentration changes with time. The latter is the domain where the sorption isotherm formalism is used. An equilibrium sorption isotherm cannot be used to describe processes with slow reaction kinetics.

The simplest and most widely used equilibrium sorption isotherm is given by a linear relationship between the amount of solute on the solid phase \( S \) [mol/kg] and the concentration of solute \( C \) [mol/m\(^3\)] in the mobile phase according to (for the following discussion we omit the subscript \( f \) and \( p \) for simplicity):

\[
S = K_d C .
\]

Here \( K_d \) is the sorption equilibrium distribution coefficient with units [m\(^3\)/kg], which is a measure of the retardation of a migrating solute. The concept of the linear sorption
Mass transport due to a concentration gradient

isotherm is based on the following assumptions

1. the solutes are present in low concentrations,
2. the system is at equilibrium,
3. the reaction is reversible,
4. the temperature is constant, and
5. no other chemical processes are occurring\textsuperscript{14}.

This description is one of those most commonly used, because it often leads to simple analytical solutions for the transport equations. Another reason that the $K_d$-concept has survived is that for many solutes the experimental sorption data may be described well by a linear sorption isotherm. When there is no linear relationship between $S$ and $C$ other types of sorption isotherms have to be used. There are several types, some of them purely empirical, others with a certain theoretical background, \textit{cf.} Chapter VII.

The Freundlich isotherm \textbf{\cite{26FRE}} is an example of a non-linear relationship between $S$ and $C$

\[
S = KC^N \tag{XII.21}
\]

where $K \ [\text{mol}^{1-N} \cdot \text{m}^{2N} \cdot \text{kg}^{-1}]$ and $N \ [\cdot]\textsuperscript{15}$, with $0 < N \leq 1$ \textbf{\cite{80SPO2}} are constant. The linear form of Eq. (XII.21) $\log_{10} S = \log_{10} K + N \log_{10} C$ is often fitted to experimental data. The Freundlich isotherm has been widely used to model sorption of solutes by soils. A serious limitation of the Freundlich isotherm is that, as for the linear isotherm, there is no maximum amount of sorbed solute on the solid phase. At low concentrations of the mobile phase, the distribution coefficient becomes large, which means strong retardation for flowing solutes but smaller retardation at higher concentrations. The linear isotherm is a special case where the Freundlich exponent is unity.

The Langmuir isotherm \textbf{\cite{18LAN}} is another type of non-linear isotherm originally introduced to describe the adsorption of gases on different solid phases. It is given by the following formula:

\[
S = \frac{\hat{K} S_{\text{max}} \cdot C}{1 + \hat{K} C} = S_{\text{max}} \frac{C}{\frac{1}{\hat{K}} + C} . \tag{XII.22}
\]

$\hat{K} \ [\text{m}^3/\text{mol}]$, $S_{\text{max}} \ [\text{mol/kg}]$ are phenomenological coefficients. For this isotherm the underlying assumptions are:

\textsuperscript{14} This means that processes like precipitation/dissolution, ion exchange \textit{etc.} which cannot be described in terms of a linear sorption isotherm formalism, but which occur in many systems and also influence the retardation cannot be properly modelled.

\textsuperscript{15} $[\cdot]$ denotes a dimensionless quantity.
Figure XII.4: Schematic $S(C)$ vs. $C$ diagrams for the linear, Freundlich and (one site) Langmuir isotherm. For the Langmuir isotherm the linear behaviour for small concentration values is indicated in the figure.

1. the sorption capacity is restricted due to a finite number of sorption sites. The maximum sorption is reached when the surface of the solid phase is covered with a monolayer of solute molecules,

2. all sorption sites are equivalent, and

3. the rate of desorption is independent of the occupation of neighbouring sites.

For low concentration $C \ll S_{\text{max}}$, where $S_{\text{max}}$ is the saturation concentration, the Langmuir isotherm has a linear behaviour while for high concentration $S(C)$ becomes a constant $= S_{\text{max}}$. $K$ is a measure of the “bond strength” for sorbed solute on the solid phase surfaces. In the past there have been different attempts to refine the Langmuir isotherm, e.g. by introducing two different types of surface sites; one site may have a high bonding strength while the other has a lower one. Such a two-site Langmuir isotherm is given by:

$$ S = S_{\text{max}}^{(1)} \frac{C}{K^{(1)}} + C + S_{\text{max}}^{(2)} \frac{C}{K^{(2)}} + C $$

In this formula the superscripts (1) and (2) refer to the two types of site. There are experimental data supporting such a model. However, for each type of sorption site two freely adjustable parameters $K$ and $S_{\text{max}}$ occur in the sorption model and have to be determined from suitable experimental data. Figure XII.4 shows the schematic representation of the three different equilibrium sorption isotherms.
Mass transport due to a concentration gradient

The sorption description reviewed above is based on the assumption that the reaction time for sorption is much smaller than the water transit time for the REV. Therefore, kinetic effects are strongly dependent on the time scale involved and play no role for certain problems. In the frame of a safety assessment for a repository for radioactive waste, where, typically, the time spans of interest are of the order of tens of thousands of years or even more, kinetic effects with rate constants of hours or even months are completely negligible. But for small scale laboratory experiments this might not to be the case. To model slow sorption/desorption processes of a solute, it is more appropriate to use a kinetic model.

To account for sorption kinetics in transport modelling, it is common to use phenomenological relationships which may lack an adequate microscopic, deterministic representation. The most simple description is the reversible first-order kinetic sorption model given by:

\[
\frac{dS}{dt} = k_s C - k_r S ,
\]

where \( S \) [mol/kg] is again the amount of solute sorbed onto solid phase surfaces and \( C \) [mol/m\(^3\)] is the concentration of solute in the mobile phase. \( k_s \) [m\(^3\)·kg\(^{-1}\)·s\(^{-1}\)] and \( k_r \) [s\(^{-1}\)] are the rates for sorption and desorption, respectively. Eq. (XII.24) accounts for the rate of solute sorption by the solid phase as a result of the difference between the actual concentration of solute in the mobile phase and what already has been sorbed. This differential equation describes a reversible non-equilibrium sorption process. If \( k_r \) is equal to zero, no desorption of solute occurs, and the sorption process becomes irreversible. If \( k_s \) and \( k_r \) are large while \( k_s/k_r \) is finite, the equilibrium linear sorption model is obtained. If the concentration in the liquid phase is regarded as constant (\( C = \text{const.} \)), assuming that initially no solute is sorbed onto the solid phase (\( S(0) = 0 \)) and the rate for desorption is \( k_r \neq 0 \), we obtain the following analytical solution for Eq. (XII.24):

\[
S(t) = \frac{k_s}{k_r} \cdot C \left(1 - e^{-k_r t}\right) .
\]

At steady-state, or dynamic equilibrium, where \( \dot{S} = 0 \) holds for Eq. (XII.24) we get:

\[
S(t) = \frac{k_s}{k_r} \cdot C := K_d \cdot C .
\]

Hence, the first order reversible sorption kinetic model is reduced to the linear isotherm with \( K_d := k_s/k_r \).

If sorption is limited one obtains a special case of a first order kinetic model:

\[
\frac{dS}{dt} = \tilde{k_s} (S_{\text{max}} - S) \cdot C - k_r \cdot S .
\]

In Eq. (XII.27) the sorption is proportional to the number of sites \( (S_{\text{max}} - S) \) still accessible for sorption, whereas the rate for desorption is proportional to the concentration of sorbed
solute. For $C = \text{const.}$ we get the analytical solution:

$$S(t) = \frac{\hat{k}_s}{k_r} \frac{S_{\text{max}} \cdot C}{1 + \frac{\hat{k}_s}{k_r} \cdot C} \left(1 - e^{-\left(\frac{\hat{k}_s}{k_r} + k_r\right)t}\right),$$  \hspace{1cm} (XII.28)

which in the steady-state results in the Langmuir isotherm (XII.22), if $\tilde{K} := \frac{\hat{k}_s}{k_r}$; $([\hat{k}_s] = \frac{m^3}{\text{mol} \cdot \text{s}})$.

We can also formulate a reversible non-linear kinetic equation similar to the Freundlich isotherm:

$$\frac{dS}{dt} = \hat{k}_s \cdot C^N - k_r \cdot S$$  \hspace{1cm} (XII.29)

Eq. (XII.29) describes sorption processes where the forward reaction is non-linear and the reverse reaction is linear. Again, $\hat{k}_s \text{[mol}^{1-N} \cdot \text{m}^{3N} \cdot \text{kg}^{-1} \cdot \text{s}]$ and $k_r$ are rate coefficients and $N$ a dimensionless quantity. In principle, $\hat{k}_s$ and $k_r$ need not be constant and may be dependent on the solute concentration of the liquid phase. The isotherm for constant solute concentration $C$ of the mobile phase is equal to:

$$S(t) = \frac{\hat{k}_s}{k_r} \cdot C^N \left(1 - e^{-k_r \cdot t}\right)$$  \hspace{1cm} (XII.30)

and, as before, at steady-state, i.e. $\dot{S} = 0$ holds, the Freundlich isotherm (XII.21) is obtained. In this case the Freundlich isotherm coefficient $K$ is the ratio of the rate coefficients $\hat{k}_s/k_r$.

Finally, we briefly mention the kinetic product model proposed by Enfield [74ENF]:

$$\frac{dS}{dt} = a \cdot C^b \cdot S^d$$  \hspace{1cm} (XII.31)

where $a$, $b$ and $d$ are phenomenological constants. There is no theoretical foundation for this expression which was empirically found by modelling the mobility of phosphorus in soil. Like the Freundlich isotherm it does not limit the sorption to a maximum value. Because no desorption rate occurs in this formula, it may be regarded as an irreversible sorption equation.

Although a number of other kinetic models [68GOU, 81AND/RUB] exist, we will not discuss them here. The intrinsic value of a particular sorption model is strongly dependent on the type of transport problem being investigated. Many problems may be tackled with the help of a simple equilibrium model, while others may require more sophisticated, and time-dependent, models. Finally, the choice of a model suitable for describing sorption processes is dependent on the type of knowledge available and the accuracy required. It makes little sense to use a $n$-site Langmuir kinetic model, if the values for the phenomenological parameters are unknown or if transport is prevailingly advective (convective) and the sorption processes only play a minor role.
In this section we discuss the influence of an additional important transport process - molecular diffusion of a solute into the porous rock matrix, briefly called matrix diffusion. For this we have to expand our model to the so-called double porosity medium concept. So far we have assumed that transport of a solute happens only within a water saturated porous medium or within a water-carrying fracture. Such a fracture could be considered as open or as partially filled with altered rock material, e.g. clay minerals or sand grains, and with a flow porosity $\varepsilon_f \ [\text{ - }]$ between 0 and 1. Now, we will assume that a solute is allowed to diffuse into the connected pore space of the host rock surrounding a water bearing fracture and altered by geological processes. Such a domain for molecular diffusion is characterised by the matrix porosity $\varepsilon_p \ [\text{ - }]$ with values, again between zero and unity and we speak now of transport of the solute in a double porosity medium. However, the dual porosity model is also widely used in non-fractured media. Hence, advection is not coupled automatically to fracture flow. In the double porosity medium concept, the fluid phase is divided into one mobile and one immobile part, with a diffusive mass transfer between them as the consequence of a difference in the solute concentration between the mobile and the immobile regions. The dual porosity medium model can be extended by introducing additional processes such as instantaneous mass exchange described by a linear or non-linear sorption isotherm in both the mobile and the immobile phases, and by introducing radioactive decay for non-stable solutes.

As a first step we will derive the system of coupled transport equations - one for transport in the fracture and the second for the molecular diffusion in the adjacent rock matrix. We will neglect dispersive effects in the fracture to demonstrate and discuss the influence of matrix diffusion on solute transport. We will first consider unlimited matrix diffusion of sorbing solutes, where the boundary in the rock matrix is infinitely far away from the interface fracture/porous rock, so that boundary effects play no role. This makes the mathematical treatment of the transport equations relatively simple. Then we will discuss limited matrix diffusion and also present a useful and simple approximation of matrix diffusion, the effective surface sorption approximation. Finally we will reintroduce dispersion and demonstrate the power, but also the limitations of this concept, on a few selected examples where the double porosity medium approach is confronted with experimental data.

Let us start with the derivation of the transport equations for a double porosity medium. According to the mass conservation equation, see e.g. [91BEA/BAC], for the variation in time of the total concentration of a species $i$ in a porous medium we can write:

$$ \frac{\partial C^i}{\partial t} = - \sum_{\alpha} \vec{\nabla} \cdot \text{flux}_\alpha - \text{sinks + sources} . \quad (\text{XII.32}) $$

The total flux is the sum of different terms, one term describing advection, another representing dispersion etc. To take solute/rock interactions into account, it is useful to split the total concentration of species $i$ into

a) a mobile part $C^i_f \ [\text{mol/cm}^3]$; the concentration of species $i$ in the liquid phase
and

b) an immobile part $S_i^f$ [mol/m$^2$] which is the amount of species $i$ per unit area of solid phase:

$$\frac{\partial C_i^f}{\partial t} = \frac{\partial}{\partial t} \left[ \varepsilon_f C_i^f + \xi_f S_i^f \right]. \quad (XII.33)$$

$C_i^f$ is the ratio of dissolved amount/quantity of species $i$, and the volume accessible for the flowing liquid; $S_i^f$ is given by the ratio of absorbed species $i$, and the surface accessed by the flowing liquid. $\varepsilon_f$ [-] denotes the flow porosity and is the ratio of the volume of flowing liquid and total volume (the latter being the sum of volume of flowing liquid and volume of solid phase). $\xi_f$ [m$^{-1}$] is the specific sorbing surface of the water-conducting zone$^{16}$ and is given by the ratio of sorbing surface and total volume of the water conducting zone.

Eq. (XII.32) is written in form of two coupled partial differential equations: one equation for transport in the water conducting zone and another equation for the transport in the rock matrix adjacent to the fracture.

The transport equation for a volume element of the water conducting feature is given by:

$$\frac{\partial}{\partial t} \left[ \varepsilon_f C_i^f + \xi_f S_i^f \right] = \boldsymbol{\nabla} \cdot \varepsilon_f \left[ D \cdot \nabla C_i^f \right] + \varepsilon_f \left[ \frac{d\bar{F}_f}{dV_f} \cdot \varepsilon_p D_i^p \cdot \nabla C_i^p \right]_{\text{interface}} + Q_i^f \quad (XII.34)$$

and that for a volume element of the matrix by:

$$\frac{\partial}{\partial t} \left[ \varepsilon_p C_i^p + (1 - \varepsilon_p) \rho S_i^p \right] = \boldsymbol{\nabla} \cdot \varepsilon_p D_i^p \cdot \nabla C_i^p + Q_i^p. \quad (XII.35)$$

The left hand side of Eq. (XII.34) describes the variations with time $t$ of the total concentration of species $i$ in the liquid phase $C_i^f$ and on solid phase $S_i^f$.

$Q_i^f$ represents a net source/sink term (mass per unit volume of the water conducting zone and unit time); $Q_i^p$ in Eq. (XII.35) a net source/sink term (mass per unit volume of porous rock and unit time) respectively, e.g. radioactive decay and ingrowth in the case of a nuclide chain.

The first term of the right hand side is minus the divergence of the flux in the water-conducting zone and is composed of

a) a flux term for the hydrodynamic dispersion $\vec{j}_{\text{disp}} = -\varepsilon_f D \cdot \nabla C_i^f$, where $D$ in general is a second rank tensor taking into account molecular diffusion and the fact that the direction of the dispersive flux is not only determined by the concentration gradient but also by the geometry of a possible fracture infill and $16$ $\xi_f$ is the sum of the flow wetted surface of a possible fracture infill and the fracture surface itself. Therefore, only those parts of the fracture surface which are not covered by fracture infill and not part of the rock pore space are considered.
b) a flux term representing advection \( \vec{j}_{adv} = + \varepsilon_f \vec{v}_f C_i^f \), where \( \vec{v}_f \) is the velocity vector of the liquid flow field.

A sink/source term describing the diffusive mass transfer of species \( i \) across the interface between the water-conducting zone and the porous rock matrix is given by

\[
-\varepsilon_f \left[ \frac{d\vec{F}_f}{dV_f} \cdot \varepsilon_p \vec{D}_p^i \cdot \vec{\nabla} C_p^i \right] \bigg|_{\text{interface}},
\]

with the second rank diffusion tensor \( \vec{D}_p^i \) taking into account that the direction of the diffusive flux is not only given by the concentration gradient, but also by the rock pore geometry. In this expression \( \frac{d\vec{F}_f}{dV_f} \) is a vector representing the ratio of the surface area of the water conducting and altered rock zone, and the volume element of the water conducting zone. Its orientation is perpendicular to the surface element and points towards the altered rock zone. In the case of a planar fracture geometry this ratio is \( 1/b \) where \( b \) [m] is half of the fracture aperture. The factor \( \varepsilon_f \) takes into account that, due to partial coverage of the interface surface by a fracture infill\(^{17} \), only the fraction \( \varepsilon_f^{18} \) of the altered zone is accessible for diffusion\(^{19} \). The matrix porosity \( \varepsilon_p \) [-] is equal to the ratio of volume of stagnant liquid and total volume. \( C_p^i \) [mol/m\(^3\)] is the amount of dissolved species \( i \) per unit volume of stagnant liquid. This term links the transport equation for advection and dispersion (XII.34) with that for matrix diffusion (XII.35).

At this point a problem could arise because the diffusive outflux across the interface is given by

\[
\vec{j}_f^i = + \varepsilon_f \varepsilon_p \vec{D}_p^i \cdot \vec{\nabla} C_p^i \bigg|_{\text{interface}}
\]

and the diffusive influx in the matrix by

\[
\vec{j}_p^i = - \varepsilon_p \vec{D}_p^i \cdot \vec{\nabla} C_p^i \bigg|_{\text{interface}}
\]

hence, \( -\vec{j}_f^i \neq \vec{j}_p^i \). Although the flux \( \text{[mol/m}^2\text{s]} \) is not continuous at the interface, mass is conserved, since the mass flow per total volume \( \dot{M}_f^i \) [mol/m\(^2\cdot\text{s}\)] is equal to that in the porous rock zone \( \dot{M}_p^i \)

\[
\dot{M}_f^i = - \frac{d\vec{F}_f}{dV_f} \vec{j}_f^i = \left( \varepsilon_f \frac{d\vec{F}_f}{dV_f} \right) \vec{j}_p^i = \dot{M}_p^i .
\]

In this equation the factor \( \left( \varepsilon_f \frac{d\vec{F}_f}{dV_f} \right) \) takes into account the restricted portion of porous rock matrix available by diffusion.

\(^{17}\) For simplicity the fracture infill is considered as being not porous. Otherwise, a third type of porosity has to be taken into account and a third transport equation would be necessary to describe contaminant transport from the flowing liquid into the fracture infill.

\(^{18}\) The term \( \varepsilon_f \) represents the ratio of (uncovered) fracture surface accessible to matrix diffusion and total fracture surface and is approximated - for simplicity - by the flow porosity \( \varepsilon_f \).

\(^{19}\) This may be a reasonable assumption if pores which are blocked by a fracture infill for diffusion from the fracture interface cannot be reached by diffusing solute via unblocked pores. However, if pore interconnection and fast diffusion in the flow direction allow such blocked pores to be reached, the factor \( \varepsilon_f \) has to be omitted.
Modelling Solute Transport Using the Double Porous Medium Approach

Figure XII.5: Sketch of the influence of a possible fracture infill in the water-conducting zone on matrix diffusion. In the upper part, matrix diffusion is reduced due to covering of matrix pores by the fracture infill. Whether such a picture is a realistic representation will depend on the system being considered. However, from a safety assessment point of view it is certainly conservative. In the lower part, the whole matrix is accessible to matrix diffusion due to pore interconnections in the matrix. In such a case the leading factor $\varepsilon_f$ of the sink/source term for diffusing transfer across the interface in Eq. (XII.34) has to be dropped.

The second transport Eq. (XII.35) represents diffusive transport of a species $i$ into stagnant water of the connected pore space of the altered rock matrix, where $\rho$ [kg/m$^3$] is the averaged solid phase density, and $S_p^i$ [mol/kg] the ratio of the mass of absorbed species $i$ in the rock matrix and the unit mass of porous rock.

For the following considerations we will make some principal assumptions and approximations. It is clear that they have to be formulated differently for different physical problems. Very often it is not necessary or, due to the lack of appropriate data, it is useless to attempt to develop a full three-dimensional formalism. In such a case a two- or even one-dimensional description may be sufficient to encompass the most relevant mechanisms and processes.$^{20}$

$^{20}$ In principle, such conceptual restrictions and approximations have to be estimated quantitatively
Mass transport due to a concentration gradient

Figure XII.6: The (x,z)-geometry for transport in a fractured rock. Advection/dispersion takes place in z-direction and matrix diffusion in x-direction. The fracture aperture is $2b$. A limitation on matrix diffusion could result if a hydrothermal altered zone beneath the fracture is embedded in a zone of fresh unaltered rock with very low porosity being considered in the model as non-porous. The porosity of the altered zone can easily be an order of magnitude larger than that of the non-porous rock zone.

In Figure XII.6 we have sketched the geometry for flow and transport in a planar fracture. However, in nature, fractures are neither planar nor do they extend as single fractures over the whole distance to be considered (see also Figure XII.1).

Let us - with the help of Figure XII.6 - specify the underlying assumptions and approximations, providing the basis for a simplification of the transport problem.

- Perpendicular to the fracture plane, in x-direction in Figure XII.6, hydrodynamic dispersion (molecular diffusion only if there is no fracture infill) is responsible for fast mixing of the solute so that the concentration distribution perpendicular to the fracture plane can be approximated by an averaged concentration. Therefore we

or, at least, motivated qualitatively. This means, in a rigid sense, that results from, say, a one-dimensional model have to be compared with results from two- or three-dimensional models. In certain disciplines such comparisons between competing models were made periodically within international benchmarking studies such as, e.g., INTRACOIN [86INT].
Modelling Solute Transport Using the Double Porous Medium Approach

assume that the fracture aperture is much smaller than its length.

- To restrict the flow within the fracture to a 1D-problem we further assume that
  the solute is released uniformly along the y-axis resulting in a zero concentration
  gradient in this direction.

- In the matrix we only consider diffusive processes occurring perpendicularly to the
  fracture. This approximation is surely reasonable because of the much lower hy-
  draulic conductivity, if transport in the fracture is much faster than in the matrix.
  The volume of the porous rock matrix, accessible to diffusion may be limited or
  unlimited.

- Very often, molecular diffusion can be neglected along the flow path (in z-direction),
  when compared to mechanical dispersion and advection, i.e., the Peclet number
  (XII.18) is much larger than unity.

Thus the water velocity vector along the flow path is reduced to \( \nu_f \); the second rank
tensor for the hydrodynamic dispersion is degenerated to the mechanical dispersion only
and this is represented by a single scalar quantity according to Eq. (XII.4)

\[
D \approx a_L \nu_f ,
\]

where \( a_L [m] \) is the longitudinal dispersion length.

In order to calculate the time- and space-dependent concentration in the water-
conducting feature \( C^i_f \) and in the stagnant pore water of the rock matrix \( C^i_p \), reasonable
assumptions about the relationship between the concentration in the mobile phase \( C \) and
the concentration on the solid phase \( S \) have to be made. For host rocks considered in a
safety assessment of a repository for radioactive waste, water velocities are of the order
of a few meters per year, hence very small; and thus, typical transport times (neglecting
retarding mechanisms at all) are of the order of hundreds of years. Sorption kinetics in
such a case certainly plays a minor role; however, kinetics may become important when
modelling laboratory experiments on a much smaller time scale.

- Therefore let us, for the sake of simplicity, assume that sorption kinetics plays no
  role, i.e. we assume instantaneous sorption equilibrium with a sorption isotherm of
  the form:

\[
S^i_{f,p} = f \left( C^i_{f,p} \right)
\]

(XII.40)

where \( f(C) \) may be any function, which in general has different forms for the fracture
and the matrix.

Considering these additional approximations and introducing Eq. (XII.40) into the set of
coupled transport equations we get:

\[
\frac{\partial C^i_f}{\partial t} = \frac{1}{R_f^i(C_f^i)} \left[ a_L \nu_f \frac{\partial^2 C^i_f}{\partial z^2} - \nu_f \frac{\partial C^i_f}{\partial z} + \frac{1}{b} \varepsilon_p D^i_p \frac{\partial C^i_p}{\partial x} \bigg|_{x=b} + Q^i_{f} \right]
\]
Mass transport due to a concentration gradient

\[ \frac{\partial C^i_p}{\partial t} = \frac{1}{R^i_p(C^i_p)} \left[ D^p \frac{\partial^2 C^i_p}{\partial x^2} + \frac{Q^i_p}{\varepsilon_p} \right] \]  (XII.42)

where we used the following abbreviations for the concentration dependent retardation functions \( R^i_f(C^i_f) \) and \( R^i_p(C^i_p) \)

\[ R^i_f = 1 + \frac{\xi_f d(C^i_f)}{\varepsilon_f} \]  (XII.43)

\[ R^i_p = 1 + \frac{1 - \varepsilon_p}{\varepsilon_p} \rho \frac{d(C^i_p)}{d(C^i_p)} \]  (XII.44)

In the case of a linear sorption isotherm of the form \( S(C) = K \cdot C \) where \( K = \text{const.} \), for the retardation functions (XII.43) and (XII.44) we get the following constants:

\[ R^i_f = 1 + \frac{\xi_f K^i_a}{\varepsilon_f} \]  (in the fracture)  (XII.45)

\[ R^i_p = 1 + \frac{1 - \varepsilon_p}{\varepsilon_p} \rho K^i_d \]  (in the matrix),  (XII.46)

where \( \xi_f/\varepsilon_f [\text{m}^{-1}] \) is the sorbing surface of the water conducting zone per unit volume of flowing water; \( K^i_a [\text{m}] \) is the surface based and \( K^i_d [\text{m}^3/\text{kg}] \) the volume based sorption equilibrium distribution coefficients. For more complicated isotherms as, e.g. the Freundlich or Langmuir isotherms (Figure XII.7), one must use concentration dependent retardation functions. Hence different parts of a migrating solute plume will move with different rates and its shape will change with time even when neglecting dispersive effects and matrix diffusion. Often, solutes have a finite natural (stable) background concentration in the transport domain. This is assumed to be constant in time and space. Therefore the cumulative solute concentration \( C_{\text{total}} = C_{\text{solute}} + C_{\text{background}} \) enters the equations for the retardation functions, thereby avoiding the unrealistic special feature of the Freundlich isotherm that \( R(C) \) becomes infinitely large for concentrations approaching zero.

Because both transport equations are first order in time and second order in space, we have to specify for each differential equation one initial and two boundary conditions depending on the physical problem at hand.

The following is used as a common initial condition for both differential equations:

a) \[ C^i_f(z,t) = C^i_i(z,x,t) = C^i_{\text{background}} ; \ t \leq 0 \text{ and } \forall z, x , \]  (XII.47)

meaning that the whole domain of interest has originally a certain solute concentration which may, of course, be zero. As examples, we mention the \(^{235}\text{U}\) and \(^{238}\text{U}\) content of groundwater flowing through crystalline (granitic) rock.
Figure XII.7: The qualitative behaviour of the retardation functions $R(C)$ for three often used isotherms as depicted in the diagrams.

The continuity condition is as follows:

b) At the interface fracture/porous (altered) rock matrix, we assume continuity in the concentration; this is given by:

$$C_j^i(z, t) = C_p^i(z, b, t) \quad \forall z ; t > 0 \quad \text{(XII.48)}$$

and continuity in flow (but not in the flux) is implicitly included in Eq. (XII.34) and (XII.41), respectively.

The boundary conditions are as follows:

c) In the porous rock matrix, we choose a no-flow boundary condition at a certain distance $b + d$ [m]; $d$ being the maximum depth for matrix diffusion:

$$D_p^i \frac{\partial C_p^i}{\partial x} \bigg|_{x = b + d} = 0 \quad \forall t \quad \text{(XII.49)}$$

The matrix diffusion is limited if a finite value is assumed for $d$, so that for sufficiently long time scales the whole accessible rock matrix becomes saturated. If $d$ is so large that only parts of the porous rock close to the interface are invaded by the solute during the time span considered, we have unlimited matrix diffusion. (A limitation of matrix diffusion could result from the presence of a hydrothermally altered zone beneath the fracture embedded in a zone of fresh, unaltered rock with very low porosity which in the model is considered as non-porous.)

552
Mass transport due to a concentration gradient

With the conditions (XII.47) - (XII.49) the second transport equation - the diffusion equation - can be solved; the corresponding boundary conditions for the transport equation in the fracture must also be fixed:

d) At the inlet - this means at the upstream boundary - we use the following form of the mixed von-Neumann/Dirichlet (also called Fourier type of) boundary condition specifying the solute flux:

\[
\left( C_i^f - a_L \frac{\partial C_i^f}{\partial z} \right) \bigg|_{z=0} = f(t) \cdot \Theta (T_L - t) \quad ; t > 0 .
\] (XII.50)

In this expression \( \Theta(w) \)

\[
\Theta(w) = \begin{cases} 
0 & ; w < 0 \\
1 & ; w \geq 0
\end{cases}
\] (XII.51)

is the Heaviside step function and \( f(t) \) is a time-dependent input function with units [mol/m³] which describes the release of the solute. \( T_L \) [s] is the release time for the solute (or species \( i \)). The Heaviside step function switches the release function \( f(t) \) during the period \([0, T_L]\).

e) At the downstream boundary, there are different possible boundary conditions: if the transport domain is considered as a semi-infinite medium \([0, \infty)\) a zero concentration boundary condition is often used.

\[
\lim_{z \to \infty} C_i^f(z, t) = 0 \quad ; \forall t .
\] (XII.52)

This boundary condition may also be used for the solute breakthrough in a field experiment where, at \( z = L \) (\( L \) finite), the solute becomes strongly and instantaneously diluted by uncontaminated fracture water.

Another possible boundary condition is the zero dispersive flow condition which corresponds to a free outflow at the outlet at \( z = L \):

\[
a_L \frac{\partial C_i^f(z = L, t)}{\partial z} = 0 \quad ; \forall t .
\] (XII.53)

This boundary condition may be appropriate for modelling column experiments but may also be consistent with a solute transfer to a non-dispersive porous medium.

In most cases it is not possible to obtain an analytical solution of the coupled system of partial and, in general, non-linear differential Eqs. (XII.41) and (XII.42) (for analytical

---

\( \text{A boundary condition is of the von-Neumann type, if the flux in direction normal to the bounding surface of the physical system is known. If the value of the quantity on the boundary is specified, then we have a boundary condition of the Dirichlet type. However, also a mixture of both types of boundary conditions is possible.} \)
Modelling solute transport in fractured porous media

solutions, see also [81TAN/FRI, 82SUD/FRI, 85AHN/CHA]). Therefore it is necessary to solve the system of equations numerically. In principle, it is possible to obtain solutions with the help of a number of numerical methods such as finite differences, finite elements, spectral method, random walk, or with the help of the method of line approximations. For certain methods (e.g. finite differences, method of lines, etc.) one has to take into consideration that the system of partial differential equations may be stiff, especially if processes with very different time scales are taken into account, e.g. when chemical reactions are included in the transport problem.

Here, we do not want to go deeper into detail; for further information the reader is referred to textbooks on numerical mathematics, especially for solving partial differential equations of the parabolic type [82LAP/PIN, 93VRE/KOR].

XII.3.6. Effects of matrix diffusion and the effective surface sorption approximation

In a former section we saw that sorption processes still cannot be explained sufficiently well; hence, assumptions on the reversibility and rate of equilibration are made. The sorption capacity and distribution ratio for different solutes and different rocks are in general measured in small scale laboratory experiments (batch sorption experiments). These data are then used to estimate - often via an isotherm formalism - the retardation for a given solute in the rock. For fractured porous rock it is assumed that flow takes place mainly in more or less open fractures, and that the solute only interacts with the fracture surfaces. Possible penetration of the solute into the rock is neglected, and hence, fluid transport through the intact rock matrix between these fractures is also neglected. Retardation in such a case is due to surface sorption. However, with this description the retardation capacity of the rock may be considerably underestimated, because microfissures, connected or unconnected pores do exist even in very dense rocks, such as crystalline rocks (see also Figure XII.1). Solutes not only flow with the groundwater in connected fractures, but also diffuse into the adjacent rock pores. Diffusion of a solute from fractures where the liquid is flowing into such water-filled micro-fissures and dead-end pores acts as a sink for a solute, because rock pores temporarily store the solute. Depending on the solute concentration in the fracture, the concentration gradient in the matrix may change its sign with time, and the diffusion direction then points towards the fracture, showing that the rock matrix can also act as a solute source. The solute may be sorbed on inner surfaces of the pore space and micro-fissures. Both processes, diffusion into the rock matrix and sorption of the solute onto the inner surfaces, slow the rate of migration of the solute and are therefore additional mechanisms for retardation and dilution of the solute concentration in the water-conducting system.

Matrix diffusion has been discussed in connection with groundwater dating [75FOS], in the petroleum engineering literature with the exploitation of oil reservoirs, but has also gained much attention in the context of radioactive waste disposal. Non-sorbing species may penetrate a few tens of centimetres of crystalline rock matrix, if the contact time exceeds 1000 years; however, strongly sorbing species penetrate only fractions of a millimetre in the same time span. Matrix diffusion can enhance the retardation by many
Matrix diffusion

orders of magnitude with respect to retardation by surface sorption only, especially when the diffusion process is combined with a high sorption capacity on the inner surfaces of the rock matrix.

Let us discuss, more quantitatively, how matrix diffusion affects solute transport for a simplified transport problem. We will study the influence of (unlimited) matrix diffusion taking into account only one-dimensional advection and neglecting dispersive effects. For simplicity, the solute is assumed to sorb linearly onto fissure surfaces and pore surfaces of the adjacent rock. Fracture infills and additional sinks for the solute, e.g. radioactive decay, will be neglected for the purpose of simplicity. The geometry of the model (see also Figure XII.6), the transport Eqs. (XII.41), (XII.42), the initial (XII.47) and the boundary conditions (XII.49), (XII.50), (XII.52) are described in the previous section.

The solutions of the two transport equations are obtained by using the Laplace transformation technique. Here, we do not go deeper into detail of the formalism and only mention the results. Both solutions are linear combinations of the complementary error function \( \text{erfc} \), and one has to distinguish between three different solutions depending on whether the solute release has been terminated or not.

In the fracture we get as the solution:

\[
\frac{C_i(z,t)}{C_0} = \begin{cases} 
0 & ; \quad 0 < t \leq \beta^i z \\
\text{erfc} \left( \frac{\alpha^i z}{\sqrt{2} \beta^i z} \right) & ; \quad \beta^i z < t \leq T^i + \beta^i z \\
\text{erfc} \left( \frac{\alpha^i z}{\sqrt{2} \beta^i} \right) - \text{erfc} \left( \frac{\alpha^i z}{\sqrt{2} \beta^i z} \right) & ; \quad T^i + \beta^i z < t
\end{cases}
\] (XII.54)

and in the porous rock

\[
\frac{C_p(z,x,t)}{C_0} = \begin{cases} 
0 & ; \quad 0 < t \leq \beta^i z \\
\text{erfc} \left( \frac{\delta^i}{\sqrt{2} \beta^i} \right) & ; \quad \beta^i z < t \leq T^i + \beta^i z \\
\text{erfc} \left( \frac{\delta^i}{\sqrt{2} \beta^i} \right) - \text{erfc} \left( \frac{\delta^i}{\sqrt{2} \beta^i z} \right) & ; \quad T^i + \beta^i z < t
\end{cases}
\] (XII.55)

We have used the following abbreviations:

\[
\alpha^i = \frac{\varepsilon_p \sqrt{D^j_p R^i_p}}{b \nu_f}, \quad \beta^i = \frac{R^i_j}{\nu_f},
\] (XII.56)

and

\[
\delta^i = \alpha^i z + \sqrt{\frac{R^i_p}{D^i_p}} (x - b).
\] (XII.58)

From Eqs. (XII.54) and (XII.55) we can see that the solution in the porous rock is reached by substituting \( \alpha^i z \) by \( \delta^i \) in the expression for the relative concentration in the fracture; the solution (XII.55) is equal to the solution in the fracture for \( x \to b \).

\[\text{erfc}(x) = 1 - \text{erf}(x), \text{ where } \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \text{ and } \text{erf}(-x) = -\text{erf}(x).\]
Let us first discuss the behaviour of the concentration profile in the fracture for large transport times, i.e., when matrix diffusion becomes important. We distinguish two cases:

1. For long release times \( T^i \) (or for constant input) we can calculate the solute breakthrough time \( t^i_0 \), which is defined as the time at which the concentration in the fracture at a given position - say \( z \) - has reached half of the input concentration \( C^i_0 \). The value of the (complementary) error function is 1/2, if its argument is also approximately half. Hence for \( t^i_0 [s] \) we find:

\[
 t^i_0 \approx \frac{R^i_f}{\nu_f} z + 4.4 \tau^i_0 . \quad (XII.59)
\]

In this result the first term of the right hand side is the transport time due to advection only, and we conclude that matrix diffusion gives rise to an additional retardation of \( 4.4 \tau^i_0 \) \(([\tau^i_0] = s)\) where \( \tau^i_0 \) is given by:

\[
 \tau^i_0 = \left( \frac{z}{\nu_f} \right)^2 \left( \frac{\epsilon_p}{2b} \right)^2 R^i_p D^i_p . \quad (XII.60)
\]

2. For short release times, where \( T^i \ll t - (R^i_f/\nu_f) z \), we can expand the (complementary) error function into a Taylor series taking into account only linear terms. By means of some straightforward algebra we arrive at the following expression for the concentration in the water-conducting features:

\[
 \frac{C^i_f(z,t)}{C^i_0} \approx T^i \left[ \frac{\tau^i_0}{\tau^i_0 t} \right]^3 \exp \left( -\frac{\tau^i_0}{t - (R^i_f/\nu_f) z} \right) . \quad (XII.61)
\]

Asymptotically, this means for \( t \gg \frac{R^i_f}{\nu_f} z \) we obtain for the concentration at \( z \) in the fracture:

\[
 \frac{C^i_f(z,t)}{C^i_0} \approx T^i \left[ \frac{\tau^i_0}{\tau^i_0 t} \right]^3 \propto t^{-3/2} . \quad (XII.62)
\]

For the peak maximum at \( z \) we set the first derivative of Eq. (XII.61) with respect to time equal to zero and obtain:

\[
 t(z)^i_{f,max} \approx \frac{R^i_f}{\nu_f} z + \frac{2}{3} \tau^i_0 . \quad (XII.63)
\]

The additional retardation for the peak maximum due to matrix diffusion in the case of a short step (pulse) input is approximately six times smaller than that in Eq. (XII.59).
Matrix diffusion

According to Eq. (XII.60) the additional retardation of the peak is enhanced, if

- the square of the migration distance and/or of the matrix porosity becomes larger,
- a tracer is more strongly sorbing in the rock matrix (larger value for $R_{ip}$),
- the square of the water velocity and/or the fracture aperture becomes smaller.

The maximum of the relative concentration at $t_{f,\text{max}}$ is reached at:

$$\frac{C_{i}^{f}(z,t_{f,\text{max}})}{C_{0}^{i}} \approx 0.23 \frac{T_{i}}{\tau_{0}} \approx \frac{T_{i}}{4 \tau_{0}} \quad (\text{XII.64)}$$

and the peak reduction is enhanced, if $\tau_{0}$ becomes large (assuming that $T_{i} \ll t - \frac{R_{i}}{v_{f}} z$ holds). However, the dependence on $T_{i}$ in Eq. (XII.64) is due to the normalisation procedure only. The breakthrough curve $C_{f}^{i}(z,t)$ is dependent on the product $C_{0}^{i} T_{i}$ corresponding to the released mass of solute and not on the shape of the release function. For illustration purposes we have plotted these results in Figure XII.8.

For completeness sake we also add the expression for the peak-maximum at $(z,x)$ in the porous rock matrix for $t \gg T + \beta^{i} z$. In analogy to the formalism for the concentration profile in the fracture for the peak-maximum we find:

$$t(z,x)_{p,\text{max}} = \beta^{i} z + \frac{2}{3} \left[ \tau_{0}^{1/2} + \frac{1}{2} \sqrt{\frac{R_{i}}{D_{p}}} (x - b) \right]^{2} \quad (\text{XII.65})$$

The term $\frac{1}{6}(x - b)^{2} = \gamma^{i} [s]$ represents the matrix diffusion time and accounts for the time span to reach the maximum concentration at $x$ in the porous rock zone. Finally, the mixed term in Eq. (XII.65) accounts for the change of the concentration profile in the water conducting zone due to matrix diffusion. As with the advection time $\beta^{i} z$ and the matrix delay time $\tau_{0}$, the matrix diffusion time $\gamma^{i}$ is a third important quantity to characterise transport problems in the framework of the double porosity medium approach.

The peak-maximum for the concentration in the matrix at $t_{p,\text{max}}$ is given by:

$$\frac{C_{p}^{i}(z,x,t_{p,\text{max}})}{C_{0}^{i}} \approx 0.23 \frac{T}{\left[ \tau_{0}^{1/2} + \frac{1}{2} \sqrt{\frac{R_{i}}{D_{p}}} (x - b) \right]^{2}} \quad (\text{XII.66})$$

Finally we mention that the concept of unlimited matrix diffusion encompasses the idea that with increased time the whole rock matrix is available for the diffusing solute. The no-diffusive flux boundary condition (XII.49) states that at $|x| = b + d$ there is a plane impermeable to matrix diffusion. This means physically that solutes diffusing into the porous rock from fractures are essentially restricted to a region beneath the fracture and are reflected at that boundary. From a safety assessment point of view, limited matrix
Figure XII.8: Effects of matrix diffusion in a 1D-advection model and neglecting (longitudinal) dispersion for a non-decaying solute migrating in a semi-infinite medium. In the upper part of the figure the breakthrough curves are shown at $z$ for a rectangular input pulse of $T_i = 1$ hour (dashed line) transported a) purely advectively (solid line-rectangle, with a peak arrival time of $(R_i/v_f) z = 25$ hours) and b) taking into account also unlimited matrix diffusion. According to Eq. (XII.63) the peak maximum is shifted by $\Delta t \approx (2/3) \tau_0^i$ ($\tau_0^i = 10$ hours) and lowered to $0.23 T_i^i/\tau_0^i$. In a $\log_{10}-\log_{10}$ plot, shown in the right upper corner, the asymptotic $t^{-3/2}$ behaviour of the breakthrough curve according to (XII.62) can clearly be recognised. In the lower part of the figure the breakthrough curves for a constant input (dashed line) are plotted. First tracer arrival time is again 25 hours taking into consideration only advection. According to Eq. (XII.59) the additional retardation due to matrix diffusion is now $\Delta t \approx 4.4 \tau_0^i$. 
Matrix diffusion

Figure XII.9: The influence of (limited) matrix diffusion for a migrating stable solute taking into account only 1D-advection, 1D-matrix diffusion, neglecting dispersion, and including sorption onto fracture surfaces and onto inner surfaces of the porous rock matrix. The plots show the relative solute concentration \( C(z, x, t)/C_0 \) as a function of space and time. The fracture upstream boundary (inlet) is at the left, the downstream boundary (outlet) at the right, respectively. Shown is the solute distribution at three different times, increasing from (a) to (c). The arrows indicate the migration distance for the original rectangular input-pulse (top hat) taking into account only advection and fracture surface sorption. Plot (b) is drawn at the advection time \( t_{\text{adv}} = (R_f/|\vec{v}_f|)L_{\text{migr}} \); in plot (c) at \( t_{\text{adv}} \), four times this value. Matrix diffusion accounts for a marked spreading of the solute in the porous rock and to a strong retardation in the fracture downstream. In plot (c) also an effect of the limitation of matrix diffusion can be recognised: a finite solute concentration at the zero-diffusive flux boundary in the porous rock matrix.
Modelling solute transport in fractured porous media

diffusion is a more conservative assumption than the model of unlimited matrix diffusion and results in higher solute concentration in the fracture.

We have already seen that the solute concentration in the porous rock is a function of time and space. If the penetration depth to which the solute is allowed to diffuse is small enough, the kinetics of matrix diffusion can fairly well be ignored in comparison with the long transport times for advection and dispersion, and an effective (fracture) surface sorption approximation may be justified. The concentration in the connected pore spaces in the porous rock adjusts “instantaneously” to the concentration in the water-carrying zone. Therefore we assume a priori the continuity equation to be:

\[ C_f^i(z,t) = C_p^i(z,x,t) ; \forall z,x ; t > 0 . \]  
(XII.67)

The system of transport Eqs. (XII.41) and (XII.42) is reduced to a single partial differential equation for solute transport in the fracture with only an effective retardation factor (assuming linear sorption) which can be defined as follows:

\[ R_{\text{eff}}^i = \frac{\text{Total quantity of solute}}{\text{Quantity of solute in solution in the flowing liquid}} \]

Defining

\[ K_{\text{a}}^i \equiv \frac{\text{Quantity of solute sorbed per unit area of flow wetted surface}}{\text{Quantity of solute in solution per unit volume of solution}} \text{[m]} \]

as the surface-based sorption equilibrium distribution coefficient and analogously

\[ K_{\text{d}}^i \equiv \frac{\text{Quantity of solute sorbed per unit mass of solid}}{\text{Quantity of solute in solution per unit volume of solution}} \text{[m}^3/\text{kg]} \]

as the volume-based sorption equilibrium distribution coefficient and using

\[ \frac{\xi_f}{\varepsilon_f} = \frac{\text{Total area of flow wetted surface}}{\varepsilon_f \ast \text{Total volume of water conducting zone}} \]

\[ = \frac{\text{Total area of flow wetted surface}}{\text{Total volume of flowing liquid}} \]

\[ \frac{d}{b} \varepsilon_p = \frac{\varepsilon_f 2 d F_{\text{fracture}} \varepsilon_p}{\varepsilon_f 2 b F_{\text{fracture}}} \]

\[ = \frac{\text{Total pore volume of the matrix accessible for diffusion}}{\text{Total volume of flowing liquid}} \]

\[ \frac{\rho_{\text{solid}} (1 - \varepsilon_p) d}{b} = \frac{\varepsilon_f \rho_{\text{solid}} (1 - \varepsilon_p) 2 d F_{\text{fracture}}}{\varepsilon_f 2 b F_{\text{fracture}}} \]

\[ = \frac{\text{Total accessible mass of the rock matrix}}{\text{Total volume of flowing liquid}} \]
where $F_{\text{fracture}}$ is the surface of the water conducting zone, we get the effective retardation factor $R_{\text{eff}}^i$:

$$R_{\text{eff}}^i = 1 + \frac{\xi_f}{\varepsilon_f} K_a^i + \varepsilon_p \frac{d}{b} \left( 1 + \rho_{\text{solid}} \frac{(1 - \varepsilon_p)}{\varepsilon_p} K_d^i \right)$$

$$= R_i^f + \varepsilon_p \frac{d}{b} R_{p}^i$$

Comparing (XII.68) with (XII.45) we see that the additional term is due to limited bulk sorption which is obtained instantaneously. If there is no matrix sorption, i.e. $K_d^i = 0$ and $R_{p}^i = 1$ the additional term is reduced to $(\varepsilon_p d)/b$ representing only the amount of nuclides in the pore water. The advantage of the effective surface sorption approximation is evident: The coupled system of transport equations is reduced to a single partial differential equation for transport in the fracture requiring much less numerical expenditure.

With the help of the matrix diffusion time $\gamma_i$ (see Eq. (XII.65) ff.) we are able to estimate the times required to equilibrate the porous rock zone accessible for matrix diffusion so that the $R_{\text{eff}}^i$-concept may be used.

- If the release time $T^i$ is large compared to the matrix diffusion time $\gamma_i$, then the concentration gradient within the porous rock zone becomes flattened, and the effective surface sorption approximation may be used.

- If, however, the release time $T^i$, and the spreading due to dispersion at the downstream boundary, which is approximately given by $\frac{2a^i(z=L)}{\nu_f} R_i^f$, and the spreading due to matrix diffusion, which is approximately $1.4 \tau_0^i(z=L)^{23}$, are small compared to the matrix diffusion time $\gamma_i$, we have an indication that the porous rock zone is not equilibrated and the effective surface sorption approximation is not applicable.

Let us now discuss the effect of limited matrix diffusion and the effective surface sorption approximation with the help of a special example. Imagine a deep-lying repository for radioactive waste. Long after the final closure of the repository $^{237}\text{Np}$, and many other nuclides, will be released into the geosphere. For the following considerations we will partially adopt parameter values from a study of geospheric nuclide transport for a Swiss model repository. A release time $T = 12$ million years and a constant inlet concentration of $C_0(t) = 10^{-7}$ M is assumed and the nuclide’s half life is 2.14 million years. We assume a zero concentration boundary at $L = 2050$ m and an observation point after $z = 500$ m. For simplicity we will limit our consideration to one dimension only. In addition to advection and matrix diffusion we also include longitudinal dispersion. For the relevant transport parameters the values in Table XII.2 are assumed.

In Figure XII.10 several calculations are shown, using the transport code RANCHMD [90RAN], with varying porous rock matrix thickness $d$, as indicated in the legend.

The figure shows the impact of limited matrix diffusion on $^{237}\text{Np}$ breakthrough. A first calculation is made excluding matrix diffusion considering only advection and dispersion as

\[\text{Further information concerning the factor 1.4 can be found in [94HEE/HAD2] - Appendix 1.}\]
Figure XII.10: The effect of limited matrix diffusion on $^{237}$Np breakthrough. $d$ is the depth of the porous rock matrix. For comparison purposes the unlimited case, including also a calculation with no radioactive decay, is shown.
Matrix diffusion

Table XII.2: Values for some transport parameters used in the double porosity medium approximation (see text).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fracture aperture (no infill assumed)</td>
<td>$2b$</td>
<td>$[m]$</td>
</tr>
<tr>
<td>Longitudinal dispersion length</td>
<td>$a_L$</td>
<td>$[m]$</td>
</tr>
<tr>
<td>Water velocity</td>
<td>$\nu_f$</td>
<td>$[m/year]$</td>
</tr>
<tr>
<td>Matrix porosity</td>
<td>$\varepsilon_p$</td>
<td>$[-]$</td>
</tr>
<tr>
<td>Diffusion constant</td>
<td>$D_p$</td>
<td>$[m^2/s]$</td>
</tr>
<tr>
<td>Solid density</td>
<td>$\rho_{\text{solid}}$</td>
<td>$[kg/m^3]$</td>
</tr>
<tr>
<td>Surface-based sorption constant (in the fracture)</td>
<td>$K_a$</td>
<td>$[m]$</td>
</tr>
<tr>
<td>Volume-based sorption constant (in the matrix)</td>
<td>$K_d$</td>
<td>$[m^3/kg]$</td>
</tr>
</tbody>
</table>

the solute transport mechanisms. According to Eq. (XII.8) the spreading due to dispersion is $2\sigma_i(t) \approx \sqrt{8a_Lz/(\nu_f/R_i^2)}$ and the nuclide front reaches the observation point only after about 220 years. Therefore the spreading cannot be recognised in the figure - the trailing edge is practically vertical. For the next curve the spreading is marked both, for the rising and for the trailing parts of the curve. Although the depth of the matrix is only one millimetre, matrix diffusion also causes a decrease of the peak maximum due to the combined effect of enhanced solute retardation and radioactive decay. For increased values of the matrix penetration depth, the peak maximum is more and more lowered and shifted to later times. Due to the additional retardation through matrix diffusion, the spreading due to dispersion alone also becomes more and more pronounced. Hence, it is the interaction of dispersion and matrix diffusion which enforces the solute spreading. Furthermore, a calculation for unlimited matrix diffusion was also made. In this, the maximum concentration is lowered by another three orders of magnitude. Finally, a calculation made assuming no decay for the solute illustrates the dilution capacity of matrix diffusion: the maximum concentration is lowered by three orders of magnitude, and the peak arrival time is shifted to later times by more than two orders of magnitude. It is the additional retardation which may become very important in the frame of a safety
Modelling solute transport in fractured porous media

assessment; if transport times become large compared to the half-life of the nuclide, radioactive decay will decrease the original nuclide inventory. Finally, we would like to mention the conservative aspect of limited, compared to unlimited matrix diffusion. Solute concentrations in the fracture may be higher by orders of magnitude, if solute uptake by the matrix is restricted to a limited domain beneath the fracture.

In another series of calculations we illustrate the quality of the effective surface sorption approximation (Figure XII.11).

Solid lines in Figure XII.11 correspond to calculations including matrix diffusion and dashed lines to the effective surface sorption approximation (essa). An excellent agreement between the two models can be seen in the plot for penetration depths to, say, 10 cm. This is a consequence of the very limited volume of porous rock matrix available for molecular diffusion and the rapid equilibration between fracture water and liquid in the matrix pore space for the given length of the released nuclide pulse. However, if the porous rock beneath the fracture is not equilibrated fast enough, i.e. if the extension of this domain is comparable to the penetration depth \(x_{1\% - b}\), it is not possible to represent matrix diffusion by an effective retardation factor or function. The single porous medium approach is not applicable, because matrix diffusion is now a time-dependent transport process.

XII.3.7. Modelling methodology and further examples

In the following, we will highlight the power of the double porosity medium concept with the help of some examples; but we will also point out the principal deficiencies of the models used.

As a first example we will study the calculations for the migration experiments performed in the Grimsel underground laboratory in central Switzerland. There, for several years tracer migration experiments have been performed as a joint undertaking of NAGRA\(^{24}\), PNC and PSI [92FRI/ALE]. Their aim is to develop the know-how for field experiments under conditions comparable to those of possible sites for a radioactive waste repository and to gain a better understanding of the processes relevant to radionuclide transport in the geosphere. Some 400 m below the surface, a hydraulic dipole field is generated in a well-characterised fracture zone in a granitic rock (see Figure XII.12). A wide variety of stable and radio-tracers is used; non-sorbing tracers such as uranine, \(^3\)He, \(^4\)He, \(^82\)Br, \(^123\)I, weakly sorbing tracers such as \(^{22}\)Na and \(^{24}\)Na, and moderately strongly sorbing ones, such as \(^{85}\)Sr, \(^{86}\)Rb, \(^{137}\)Cs, ... . The migration experiments are accompanied by extensive laboratory investigations on petrography, water-rock and nuclide-rock interaction [89BRA/AKS]. Thus, values for parameters are available from independent experiments, and hence the best fit-parameter values from the migration model can be tested for consistency with the laboratory data. In addition to the experimental activities, extensive modelling work is also performed, e.g. [94HEE/HAD2, 94HEE/HAD3, 96HAD/HEE].

---

\(^{24}\) NAGRA: National Cooperative for the Disposal of Radioactive Waste (Switzerland),

PNC: Power Reactor and Nuclear Fuel Development Corporation (Japan),

PSI: Paul Scherrer Institute (Switzerland).
Figure XII.11: Comparison of the effective surface sorption approximation essa (dashed lines) with calculations assuming matrix diffusion (solid lines) for various penetration depths $d$. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_xii_11.png}
\caption{Comparison of the effective surface sorption approximation essa (dashed lines) with calculations assuming matrix diffusion (solid lines) for various penetration depths $d$.}
\end{figure}
Figure XII.12: Schematic overview of the Grimsel migration experiment showing the laboratory drift, some of the boreholes drilled for the hydrogeological characterisation and the tracer experiments. Within the migration shear zone an artificial dipole flow field between injection and extraction borehole is established as depicted in the figure.

have chosen data for a conservative tracer - uranine - and a moderately sorbing tracer - strontium - to illustrate the effects of limited matrix diffusion.

As can be seen in Figure XII.13, good reproduction of the experimental data can only be obtained by including matrix diffusion in the model.
Matrix diffusion

Figure XII.13: Effect of matrix diffusion on tracer breakthrough for a conservative (uranine) and for a weakly sorbing tracer (strontium). (Figure according to [94HEE/HAD2]). The curves refer to the best-fits with matrix diffusion. The calculations demonstrate that it is cogently necessary to include this process in the model.
Modelling solute transport in fractured porous media

From the fitting procedure the following values were obtained:

a) from modelling the conservative tracer (uranine)\(^{25}\):

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2b)</td>
<td>[m]</td>
<td>(9.3\pm4.6\cdot10^{-5})</td>
</tr>
<tr>
<td>(a_L)</td>
<td>[m]</td>
<td>(25\pm5\cdot10^{-2})</td>
</tr>
<tr>
<td>(\varepsilon_p)</td>
<td>[-]</td>
<td>(6.2\pm0.8\cdot10^{-2})</td>
</tr>
<tr>
<td>(D_p)</td>
<td>([m^2/s])</td>
<td>(2.5\pm1.2\cdot10^{-11})</td>
</tr>
</tbody>
</table>

For comparison purposes also values for the rock porosity and the diffusion constant deduced from geological investigations are presented at the right end of the table (taken from [94HEE/HAD2] - Appendix 5).

b) from modelling of the sorbing tracer (strontium) we obtain in addition\(^{26}\):

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_d)</td>
<td>([m^3/kg])</td>
<td>(21\pm38\cdot10^{-3})</td>
</tr>
</tbody>
</table>

This value can now be compared with those from independent, e.g. batch sorption experiments for \(K_d\) (Table XII.3). It may be questioned if it is reasonable to compare values from experiments which have been made with so different time and concentration scales. In the case of strontium, independent measurements for \(K_d\) were performed and are listed below together with the value obtained from the Grimsel migration experiment.

The \(K_d\) values are consistent within the estimated uncertainty range indicating that for “nuclides sorbing rapidly, and not too strongly, and exhibiting a reversible cation exchange process on fault gouge, the laboratory sorption coefficients can reasonably well

\(^{25}\) No infill in the water conducting zone was assumed. \(\varepsilon_p\) and \(D_p\) could be determined separately because the breakthrough curve was measured long enough until the prominent bump at the end of the experiment indicating limited matrix diffusion. The parameters are median values of log-normal distributions and the errors correspond to one geometric standard deviation - expressing therefore relative uncertainty limits.

\(^{26}\) The parameters determined with uranine are assumed to be valid also for strontium hence, leaving \(K_d\) as the only freely adjustable parameter.
Table XII.3: Comparison of the volume-based sorption equilibrium distribution coefficient, $K_d$, for strontium from different laboratory experiments and from the Grimsel migration experiment. The large positive errors of the $K_d$ values from the batch and the rock-water interaction experiments originate in the extrapolation of the laboratory results to the conditions in the migration fracture. The errors of the $K_d$ from the migration experiment correspond to one geometric standard deviation (taken from [94HEE/HAD2]).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$K_d \cdot 10^3$ [m$^3$/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch (grain size &lt; 63 µm)</td>
<td>41±39</td>
</tr>
<tr>
<td>Batch (grain size &lt; 250 µm)</td>
<td>25±22</td>
</tr>
<tr>
<td>Batch (loosely disaggregated)</td>
<td>13±19</td>
</tr>
<tr>
<td>Rock-water interaction (loosely disaggregated)</td>
<td>8±8</td>
</tr>
<tr>
<td>Migration experiment</td>
<td>21±38</td>
</tr>
</tbody>
</table>

be extrapolated to field conditions. Adequate care in selecting and preparing the rock sample is, of course, a necessary requirement” [94HEE/HAD2]. Note, for strontium it was not possible to determine values for $\varepsilon_p$ and $K_d$ because the breakthrough curve was not monitored long enough until the bump in the trailing edge indicating limited matrix diffusion appeared.

In order to illustrate the predictive qualities of the double porosity medium approximation the breakthrough curves for uranine and cesium were calculated for other experimental conditions. These new experiments were then made in the same fracture but using a smaller and faster dipole flow field where the transport times were much shorter. The values of the sorption distribution coefficient $K_d$ and the parameters characterising the fracture and matrix from the modelling within the longer dipole field were used. In Figure XII.14 the predictions and the experimental data are compared with each other.

For uranine the agreement is excellent, indicating that the average fracture properties for the small dipole flow field are the same as for the longer ones and that the model is consistent. However, for cesium the fast breakthrough was not predicted at all. A calculation with a smaller $K_d$-value could fairly well reproduce the rising edge but failed completely to describe the trailing part of the breakthrough curve. This fact indicates that neglecting slow sorption kinetics for cesium (not covered by effects of matrix diffusion) might be the reason for the marked discrepancy between model and observed data. In experiments in a slower and longer dipole field, the effects of sorption kinetics could not
Figure XII.14: Prediction of uranine and cesium breakthrough in the Grimsel migration experiment using the double-porosity medium concept for a smaller and faster dipole flow field. The transport parameters were calibrated first on breakthrough curves for both tracers in the same fracture but in a longer dipole field. The experimental data are shown as circles or crosses. For uranine there is an excellent agreement between the model and the experimental data. This is not the case for cesium where the model does not match the measurements, especially not in the rising part. The shape of the peak region of the cesium breakthrough curve may indicate slow sorption kinetics.
Matrix diffusion

be observed. For a safety assessment of a nuclear waste repository, sorption kinetics would certainly be less important due to the much longer time-scale being involved here.

Experiments similar to the ones at the Grimsel underground laboratory were performed in Sweden in the early 80’s with extensive migration experiments at a test site near lake Finnsjön 140 km north of Stockholm. The tracer tests were made in granitic rock at a depth of about 100 m in a highly permeable fracture zone. One of the migration distances was about 30 m, and among the tracers used there were inactive iodide, strontium and cesium. The experiments are documented in detail in [81GUS/KLO, 84GUS/KLO]. In the past, several attempts to model these experiments were made, especially by teams participating in INTRACOIN [86INT]. A further detailed analysis was performed by PSI and is documented in [94JAK/HAD]. We have selected two calculations from this study as examples to demonstrate the iterative character of such modelling work. A first calculation was done using only the single-/double-porosity medium concept.

Figure XII.15 illustrates that the single-porosity medium approach reproduces the measured data only roughly and represents a somewhat ‘averaged’ behaviour. Including matrix diffusion results only in slightly different values of the fitting parameters and does not improve the overall-quality of the fit (e.g. smaller value for the $\chi^2$-merit function). Only by introducing a second preferential flow path with its own set of freely adjustable fitting-parameters do we obtain a much better representation of the experimental data, especially in the rising edge of the breakthrough curve (Figure XII.16); hence, this model seems closer to the “experimental reality”.

In order to judge a given model we have to compare the extracted best-fitting parameter values also with the model’s underlying assumptions.

As seen from Table XII.4 the value for the longitudinal dispersivity in the case of a one-flow-path system is approximately equal to the migration distance. Such a value is very large for an experiment of this type and indicates that the advection-dispersion equation may not be useful. By introducing a second flow path this quantity is reduced to a reasonable value. The study showed that it was only by including the full information of the experiment that further improvements could be reached, e.g., also pump flow variations at both boundaries - up- and downstream - had to be taken into account. Such variations in the pumping rates had a critical influence on the extracted best-fit parameter values and could partially be identified as wiggles and peaks in the experimental breakthrough curve.

We would like to finish this chapter with some remarks on the double-porosity medium approximation as it was demonstrated in this section. This approach is still used worldwide for modelling both laboratory and field experiments and for safety assessment purposes. An advantage of the concept is that it is easy to understand the underlying physics and chemistry. The model is also capable of accurately fitting even complex experiments. Past experience has shown it to be a versatile, efficient and also appropriate tool for modelling, because it covers the most important transport processes such as advection, dispersion, matrix diffusion, sorption, etc.; it is also flexible enough to take into consideration various flow geometries such as the planar fracture (parallel plate representation), vein geometry and superposition of flow paths. It is the simplicity of this concept, its
Figure XII.15: Plot of a best-fit curve for iodide breakthrough in a Finnsjö n migration experiment in the frame of a single-porosity medium approximation. Also shown are the experimental data as indicated in the legend.
Figure XII.16: A calculation using the same experimental data as in Figure XII.15 but including a second preferential flow path. The tracer breakthrough concentration in the fracture is given by the superposition of the contribution of both flow paths. The full-drawn curve is the best-fit with this model.
Table XII.4: Values of the best-fitting parameters and the minimum value for the \(\chi^2\)-merit function for two alternative calculations for iodide breakthrough in the Finnsjön migration experiment assuming either one or two preferential flow path(s). \(a^{(i)}, i = 1, 2\) are the weighting factors for each flow path; they sum up to unity. (Superscripts denote the first and second flow path.)

<table>
<thead>
<tr>
<th>Parameter (a^{(i)})</th>
<th>Unit</th>
<th>1 flow path</th>
<th>2 flow paths</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a^{(1)})</td>
<td>[-]</td>
<td>1.0</td>
<td>0.617 ± 0.031</td>
</tr>
<tr>
<td>(a^{(2)})</td>
<td>[-]</td>
<td>-</td>
<td>0.383 ± 0.031</td>
</tr>
<tr>
<td>(a_L^{(1)})</td>
<td>[m]</td>
<td>31.8 ± 9.7</td>
<td>9.47 ± 0.07</td>
</tr>
<tr>
<td>(a_L^{(2)})</td>
<td>[m]</td>
<td>-</td>
<td>8.70 ± 3.77</td>
</tr>
<tr>
<td>(</td>
<td>v_f^{(1)}</td>
<td>\cdot 10^{-4})</td>
<td>[m/year]</td>
</tr>
<tr>
<td>(</td>
<td>v_f^{(2)}</td>
<td>\cdot 10^{-4})</td>
<td>[m/year]</td>
</tr>
<tr>
<td>(\chi^2 \cdot 10^5)</td>
<td>[-]</td>
<td>0.459</td>
<td>0.242</td>
</tr>
</tbody>
</table>

Versatility and applicability to a broad variety of real-world observations in the context of solute transport in geological media, which has established the usefulness of the double porosity medium model.

XII.4. Acknowledgments

The author would like to express his indebtedness to I. Grenthe, J. Hadernann, W. Heer, and J. Pearson for reviewing and valuable criticism during the preparation of this chapter.

XII.5. Glossary

For our purposes we denote as a continuum a part of the space (body) which is occupied by mass. All quantities describing the behaviour of a body, such as the density, temperature etc., have to be continuous functions in space and time. The behaviour of a material as a whole is relevant for the investigations, and any microscopic (molecular) consideration is disregarded. This description does not reflect the real physical situation; it is only a convenient abstraction of a real world fact and permits the mathematical treatment of
physical quantities as continuous functions. In such a concept only averaged properties are taken into account and microscopic fluctuations are not considered (see also REV).

**Extensive quantities** depend on the size of the physical system. They are proportional to the system dimensions such as volume, mass, *etc.* and thus are additive. If two or more separate physical systems are combined to a unified system, then the extensive quantities are the sum of those of the constituent systems.

An **intensive quantity**, such as, *e.g.*, pressure, density, *etc.* is independent of the system dimensions. Intensive quantities are continuous functions of the space and time variable, since the values of these quantities have to be specified at each point in the system. These values may change from point to point, and such quantities are not additive.

As examples for extensive and intensive quantities we mention:

<table>
<thead>
<tr>
<th>Extensive variables</th>
<th>Intensive variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of particles $N$</td>
<td>Temperature $T$</td>
</tr>
<tr>
<td>Volume $V$</td>
<td>Pressure $p$</td>
</tr>
<tr>
<td>(total) Energy $E$</td>
<td>Chemical potential $\mu$</td>
</tr>
<tr>
<td>Entropy $S$</td>
<td>Velocity $\nu$</td>
</tr>
<tr>
<td>Internal energy $U$</td>
<td>Specific heat</td>
</tr>
<tr>
<td>Mass $m$</td>
<td>Density $\rho$</td>
</tr>
<tr>
<td>Charge $q$</td>
<td></td>
</tr>
</tbody>
</table>

A *model* is an abstraction of a real world phenomenon. In a given model, a state of a physical object, the forces which interact between physical objects, and events are represented by mathematical formulae which contain variables and constants. Such (mathematical) variables or constants represent physical quantities. In this sense a model is only a hypothesis of the temporal behaviour of a physical object under the effect of forces being totally independent and artificial to the physical objects, forces and events considered. A model incorporates a large number of assumptions or simplifications about the real world phenomena and is therefore never a complete nor an exact description of a real world phenomenon, *cf.* Chapter.

A *porous medium* is defined according to Bear and Bachmat [91BEA/BAC] as “... a portion of space occupied by heterogeneous or multiphase matter. At least one of the phases comprising this matter is not solid. They may be gaseous and/or liquid phases. The solid phase is called the solid matrix. That space within the porous medium domain that is not part of the solid matrix is referred to as void (or pore) space.”

A fracture can be seen as a part of the void space but with the property that the fracture aperture or fracture width is much smaller than its length. The aperture is an important parameter for transport modelling, although this quantity is not a constant along the fracture and may be difficult or impossible to determine. The aperture is an averaged model parameter and has nothing to do with the actual openings for transport of a solute. Fractures may be partially filled with, *e.g.*, clay minerals and other materials reducing
the real fracture width. Such infills may strongly influence the transport properties of fractures.

Matter is denoted as *homogeneous* with regard to a certain property, if this property does not vary in space, hence, is translation-invariant. If this property is independent of direction at a considered point, the medium is said to be *isotropic* at that point. Hence, it is rotation-invariant. An example of a homogeneous but anisotropic medium is a Weiss-domain in ferromagnetic materials where all the elementary magnets are aligned.

A *process* is defined as the act of changing a physical system from a given state to another. Only the initial and the final states are fixed; in general, nothing is said about intermediate states. A system in equilibrium neither changes its mass nor its energy. In other words, none of its properties changes with time.

A *REV* (Representative Elementary Volume) is the selected minimum volume of material over which a physical quantity can be averaged so that its value is not sensitive to small variations of the REV and variations of its size. The size of such a REV strongly depends on the geometry of the material and represents (generally speaking) the smallest possible volume which contains the full complexity of the physical system. In practice, it is very cumbersome to determine the size of a REV, as it is strongly site-specific. For further consideration of this problem of REV-formation we refer to literature [91BEA/BAC], and [86MAR3].

Closed systems have boundaries which are permeable for energy transfer in both directions but not for the transfer of matter. Such systems have a fixed mass and composition but a variable total energy.

Open systems are characterised by walls which allow transfer of both matter and energy in both directions, to and from the system. Such systems have neither a fixed mass and composition nor a fixed energy level.

For completeness we mention three important categories of mathematical quantities underlying the physics of transport phenomena:

1. A *scalar* is a tensor of zero order. A scalar quantity is characterised by its magnitude only and shows no direction dependence hence being specified by one single numerical value. Changing the co-ordinate system does not affect its value being an invariant. Examples of scalar quantities are concentration, pressure, density and temperature.

2. A *vector* is a tensor of the first order and is characterised by its magnitude and its direction. In a 3-dimensional space it may decomposed into three scalar quantities. Changing the co-ordinate system does not affect a vector only its components. Velocity and momentum are examples of vector quantities.

3. A *second rank tensor* is a mathematical entity which is characterised by its magnitude and two directions. A second rank tensor may be resolved into 9 scalar quantities which are dependent on the co-ordinate system; however the tensor is invariant. Diffusivity and viscosity stress are examples of tensors of the second order.