Effect of Uncertainty of Rock Properties on Radionuclide Transport by Groundwater

Implications for Performance Assessments of the Repository of Spent Nuclear Fuel in Heterogeneous Bedrock

BY

SHULAN XU
ABSTRACT


The overall objective of the current study is to develop a quantitative understanding of the effects of spatial variability in physical and geochemical properties of crystalline rock on the migration of radionuclides along a single fracture in bedrock. A stochastic model was developed to describe the transport of solutes in fractured rock. The model describes the migration of radionuclides along a one-dimensional path and includes the transversal diffusion into the rock matrix and sorption kinetics. By using a Lagrangian method of description we can extend the model to the description of a two-dimensional transport problem in single fractures.

This study presents the first analysis of the impact of heterogeneous mass transfer on the transport of radionuclides in rock fractures, where most of the relevant rock properties such as aperture, porosity, effective diffusivity, sorption capacity and maximum diffusion depth are defined as being spatially random. The stochastic analysis performed here reflects the uncertainty in our knowledge of the properties associated with a discrete sampling technique in site investigations.

Geostatistics of the main parameters was determined experimentally on a large number of rock samples taken from the Swedish crystalline basement. The knowledge of the covariance functions of the main rock properties is then used as a basis for a stochastic analysis. By combining the small perturbation approach with the spectral method the problem could be solved in terms of closed form solutions for the central temporal moments of the residence time probability density function.

In order to be able to distinguish between the effects of various mechanisms from the effects of heterogeneity on the migration of radionuclides, it was necessary to perform independent studies of the effect of the variation of the dispersion coefficient on the aspect ratio of a rectangular flow section and the effect of adsorption kinetics on the migration.

Finally, the effect of the heterogeneous rock properties on the solute transport observed in a limited number of migration experiments corresponds fairly well to the theoretical effect expected on the basis of the experimentally determined auto-covariance functions.

Key words: Radionuclide migration, heterogeneous rock property, stochastic process, spectral analysis, temporal moments, auto-covariance functions, sorption kinetics, performance assessment.

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Preface

This thesis is based on the following six papers, which are referred to by their Roman numbers in the text:


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1. Introduction

The isolation of high-radioactive waste in deep geological formations is the main option for the disposal of spent nuclear fuel in Sweden as well as in several other countries. Performance assessments of the final disposal for spent nuclear fuel include estimates of the transport of radionuclides that accidentally escape through the engineered (local) barriers. The geosphere will act as an outer barrier that retards the migration of radionuclides to the biosphere. A thorough understanding of the migration mechanisms and the effect of spatial heterogeneity of rock properties on the transport of radionuclides in fractures is therefore essential for the performance assessment. The Swedish Nuclear Power Inspectorate (SKI) initiated the present project to study the geostatistics of rock properties and its effect on the migration of radionuclides in groundwater in rock fractures. The project has been proceeding for five years.

1.1 Technical background

The main Swedish concept for the final disposal of spent nuclear fuel is based on the KBS-3 method (KBS-3, 1983), which implies that the high-level radionuclides are placed in a deep repository (500 metres) in crystalline bedrock with several engineered barriers (Fig. 1). The spent nuclear fuel is enclosed in copper canisters with an insert of cast iron. The canisters are placed in bored holes in the floor of the deposition tunnels. The canister is surrounded by bentonite which, after absorbing water and swelling, will isolate the canister from groundwater flow, hold the canister in place and retard transport of radionuclides from the canister to the surrounding rock. In a worst case scenario the engineered barriers will fail and the barrier efficiency for possible release of radioactivity then relies on the rock environment.

A Performance Assessment (PA) provides a basis for decisions on issues related to repository safety (SKI SITE-94). Such an assessment is a system analysis that includes a description of the behaviour of the repository and its surrounding environment as an integrated system. The evaluation includes hypotheses of the future evolution in terms of various scenarios under which radionuclides disposed in the repository may be released from the engineered barriers and transported through the geosphere to the biosphere. The PA analysis is complicated by the fact that the system is subject to future evolution and uncertainty. Therefore, treatment of the uncertainty and models for the description of complex systems feature prominently in the PA methodology. Safety analyses usually also consider the biosphere. In SR 97 (1999) a target variable was the long-term accumulation of different isotopes in rivers. This study focuses on the mechanism and transport phenomena related to the PA analysis of the geosphere and further limits to a single fracture.

Recent understanding of sorption kinetics and heterogeneity in the mineralogy of crystalline rock indicates that small-scale transport phenomena can be of significance to the transport of radionuclides also over larger distances in the bedrock (Selroos and Cvetkovic, 1992; Cvetkovic, et al., 1999). Moreover, Heath and Montoto (1996) presented micro-structural evidences and historical records of matrix diffusion that
support the conclusion that the matrix diffusion is limited to a narrow zone adjacent to the water conducting fractures. This limited matrix diffusion zone may also have a heterogeneous depth distribution along the transport path.

An important issue in the performance assessment of the geosphere is the inclusion of the above mentioned small-scale phenomena. This suggests that there is a need to perform basic laboratory investigations of certain crucial phenomena and include the associated knowledge in the transport analysis.

Fig. 1 The KBS-3 method for the storage of spent nuclear fuel (after SR 97, 1999).

1.2 Theoretical background

During the past decades various transport models have been developed to describe solute transport in rock fractures. The transport models include advection of solute transport along fractures and sorption is assumed to occur on the main fracture walls (e.g. Wels and Smith, 1994) as well as inside the rock matrix in combination with diffusion in the pore channels (e.g. Neretnieks, 1980). Further, the matrix diffusion is treated as having an infinite (e.g. Neretnieks, 1980) or a limited diffusion (e.g. Grisak and Pickens, 1980). Field observations in the site characterisation projects (e.g. in Stripa mine) show that there are often strong channelling effects in crystalline rocks (Abelin et al., 1985).

Based on observations, the groundwater flow is often extremely unevenly distributed. Andersson and Dverstorp (1987) used a network of discs with stochastic radius, location and orientation in space to model the channelling of flow or preferential flow paths. The model has been incorporated with a variable fracture model (Moreno et al., 1988) by Nordqvist et al., (1992) and Dverstorp et al., (1992) to evaluate the impact of
flow heterogeneity on solute transport. The model parameters for mass transfer were treated as constants.

Several studies reveal that crystalline bedrock can possess also a marked heterogeneity of various other physical and geochemical properties that potentially may have a certain impact on the transport of radionuclides in fractured bedrock. Owing to alteration and weathering of the rock matrix the porosity in the rock matrix is highly heterogeneously distributed (Sittari-Kauppi et al., 1997). Complex combinations of rock minerals and surface coatings result in spatially varying sorption capacities in water-conducting fractures (e.g. Stanfors, et al., 1999). The multirate model developed by Haggerty and Gorelick, (1995) is able to model simultaneous mass transfer with heterogeneous transport properties such as sorption rates and porosities. Recently, Cvetkovic et al., (1999) analysed the effect of heterogeneous aperture and matrix diffusion on solute transport in a single fracture in terms of two spatially random parameters, which relate to the flow field using a Monte Carlo technique based on a Lagrangian model description.

1.3 Scope of the study

The overall purpose of this study is to present the first analysis of the impact of heterogeneous mass transfer on the transport of radionuclides in rock fractures, in which most of the relevant rock properties are considered to be spatially random.

The geostatistics of the main transport properties is obtained experimentally as a basis for the analysis. The analytical solutions of the mean values of the temporal moments of the residence time probability density function (PDF) are derived by solving the stochastic model combined with a small perturbation approach and the spectral method. The analyses of the effect of heterogeneous mass transfer on radionuclide migration in a single fracture can thus be performed by decomposing the transport problem into a one-dimensional mass transfer problem and a two-dimensional flow problem using a Lagrangian method of description.

In order to differentiate the effects of various mechanisms on the migration of radionuclides, we need a thorough understanding of the parameter variability in rock, shear dispersion and adsorption kinetics. This can be obtained from independent studies of the effect of the variation of the dispersion coefficient with the aspect ratio of a rectangular flow section and the effect of adsorption kinetics on migration.

Laboratory migration experiments with tritium as tracer element provides an empirical basis for the evaluation of the transport in heterogeneous fractures. The implication of the heterogeneity of the rock properties for the radionuclide transport is addressed in practical cases of relevance to a safety assessment of a nuclear waste repository.
2. Analysis of radionuclide transport with uncertain parameters

The significant spatial variability of the rock properties has an important influence on the migration of radionuclides in fractured rocks (e.g. Dagan, 1982). Consequently, there are (at least) two important problems related to the spatial variability of rock properties, effects of the actual (real) spatial parameter variability along the transport paths and effects due to the uncertainty in our knowledge of the heterogeneous rock properties.

The heterogeneous property of the rock can be seen as a realisation of a random process. If the exact properties of the rock at each point are known, the problem can be analysed by means of a deterministic approach. However, in a deterministic description of the spatial variability we completely disregard the residual effect related to the uncertainty of the rock properties. For practical reasons, we will never be able to know the exact property of the rock at each point of the geosphere. In such a view, a property of the rock can be defined at a given geometrical point in space as the average over all possible realisations of its point value. This is called an "ensemble average" of the point value (Marsily, 1986).

Analysing an ensemble of equally probable realisations of the real case can represent the uncertainty in the solution, where the ensemble of realisations satisfies certain statistical requirements of the bedrock. Here the aim is to estimate the expected value and variance of the solution (here the solute concentration) at each point for all possible realisations of the rock properties. To do this, the stochastic model is first developed and then solved by using the perturbation approach and the spectral method.

2.1 Models of solute transport in fractured bedrock

Transport of radionuclides in a two-dimensional single fractured rock depends on advection along preferential trajectory paths in individual fractures as well as on diffusion into micro-fissures in the rock matrix and sorption on to the solid matrix (Fig. 2). By means of a Lagrangian method of description, we can decompose the solute transport problem into a two-dimensional problem, where the trajectory paths of inert water parcels are determined, and into a one-dimensional problem, where the mass transfer between the parcels and the rock matrix is determined (e.g. Cvetkovic et al., 1999).

The formulation proposed in this study is similar to that of Kunstmann et al., (1997), but it includes non-equilibrium sorption in accordance with Maloszewski and Zuber, (1990). The one-dimensional solute mass transport along a trajectory path (the dashed line in Fig.2) can be given as:

\[ \frac{\partial \tilde{c}_m}{\partial t} + \tilde{u} \frac{\partial \tilde{c}_m}{\partial \xi} = \frac{\partial}{\partial \xi} \left( \tilde{D} \frac{\partial \tilde{c}_m}{\partial \xi} \right) + \lambda \tilde{c}_m = 0 \]  

(1)

\[ \frac{\partial \tilde{c}_{sm}}{\partial t} - \tilde{e}_f \tilde{D}_{rf} \frac{\partial \tilde{c}_{sm}}{\partial \zeta} + k_s \left( \tilde{K}_s \tilde{c}_{sm} - \tilde{D} \tilde{c}_w \right) + \lambda \tilde{c}_{sm} = 0 \]  

(2)
\[
\frac{\partial \tilde{c}_m}{\partial t} - k_i \left( \frac{\tilde{c}_m - \tilde{c}_w}{\rho} \right) + \lambda \tilde{c}_w = 0
\]

where \( c \) is the concentration of the solute per unit volume of water \([kg/ m^3]\), \( c_m \) is the dissolved mass per unit volume of water \([kg/ m^3]\), \( t \) is the time \([s]\), \( \xi \) is a trajectory coordinate \([m]\), \( u \) is the advective velocity \([m/s]\) along \( \xi \), \( h \) is the fracture aperture \([m]\), the effective diffusivity \( D_e = \varepsilon_t D_p \text{ [m}^2/\text{s}]\), the pore diffusivity \( D_p = D \delta_D/\tau^2 \text{ [m}^2/\text{s}]\), \( D \) is the molecular diffusivity \([m}^2/\text{s}]\), \( \varepsilon \) is the total porosity of the rock, \( \varepsilon_t \) is the porosity of the rock matrix available for matrix diffusion, \( \delta_D \) is the constrictivity, \( \tau \) is the tortuosity, \( \rho \) is the density of the rock \([kg/ m^3]\) and \( \lambda \) is the rate of radioactive decay \([1/s]\). Further, the partition coefficient, \( K_D = (\rho/\varepsilon) k_d \), where \( k_d = (c_w/c_m)|_e \), \( c_w \) is the sorbed solute mass per unit solid mass \([kg/kg]\), the notation \( |_e \) denotes 'evaluated at equilibrium', \( k_r \) is the sorption rate coefficient \([1/s]\) and \( z \) is the coordinate \([m]\) perpendicular to the main direction of the flow.

Variables marked with a 'tilde' (~) are assumed to be spatially random in the transport direction (along the trajectory path), whereas they are constant in the lateral direction in the rock matrix \((z\text{-direction})\).

The boundary and initial conditions of a solute pulse travelling in the fracture are defined as

\[
\tilde{c}(x = 0, t) = \delta(t) \frac{M_0}{Q} \tag{4}
\]

\[
\tilde{c}_m(z = 0, t) = \tilde{c}(\xi, t) \tag{5}
\]

\[
\frac{\partial \tilde{c}_m}{\partial z} |_{z = l} = 0 \tag{6}
\]

\[
\tilde{c} (\xi, t = 0) = \tilde{c}_m(\xi, t = 0) = 0 \tag{7}
\]

\[
\tilde{c} (\xi, t = \infty) = 0 \tag{8}
\]

where \( M_0 \) is the total mass of the solute inserted into the fracture \([kg]\), \( Q \) is the water flow \([m^3/s]\), \( \delta(t) \) is the Dirac delta function \([1/s]\).

Since cations, like Cs, are adsorbed to mineral surfaces, one fraction of the ions occupies specific sites on the surface due to complexation or ion exchange and the other fraction is more weakly attracted to the surface by electrostatic interaction. The mobility of the weakly attracted ions is altered compared with the mobility of the free phase in the aqueous solution. The mobility of the ions in this weakly sorbed phase is known as surface diffusion (Skagius and Neretnieks, 1988; Eriksen and Jansson, 1996; Ohlsson and Neretnieks, 1997). If a sorbed mobile phase \( c_s \) is introduced, the model can be extended to include surface diffusion (Paper I). Fig.3 shows a schematic of the diffusivity and adsorption model.
Fig. 2 Schematic illustration of the conceptual model used to analyse the effect of matrix diffusion and adsorption kinetics on radionuclide migration.

Fig. 3 Schematic representation of the kinetic sorption and surface diffusion model.

Equations (1) and (2) are then rewritten as:

\[
\frac{\partial \tilde{c}}{\partial t} + \tilde{u} \frac{\partial \tilde{c}}{\partial \tilde{z}} - E \frac{\partial^2 \tilde{c}}{\partial \tilde{z}^2} + \lambda \tilde{c} - 2 \frac{D}{\tilde{h}} \frac{\partial \tilde{c}}{\partial \tilde{z}} \bigg|_{z=0} = 0 \tag{1a}
\]

\[
\frac{\partial \tilde{c}_m}{\partial t} - \frac{\tilde{e}}{\tilde{e}} \tilde{D}_p \frac{\partial^2 \tilde{c}_m}{\partial \tilde{z}^2} + \Psi k_r \left( \tilde{D} \tilde{c}_m - \frac{\tilde{P}}{\tilde{e}} \frac{\tilde{c}_w}{\tilde{c}} \right) + \lambda \tilde{c}_m = 0 \tag{2a}
\]

where

\[
\Omega = \frac{1 + \frac{D}{\tilde{D}_p} \frac{\rho}{\tilde{e}} k_{d1}}{1 + \frac{\tilde{D}}{\tilde{c}} k_{d1}}
\]
\[ \Psi = \frac{1}{1 + \frac{D_s k_{d1}}{\varepsilon}} \]

in which \( c_s \) is the sorbed mobile solute mass per unit solid mass [kg/kg] and \( D_s \) is the surface diffusivity [m\(^2\)/s]. Further \( k_{d1} = (c_s/c_m) \) and \( D_e = \varepsilon_i D_p + k_{d1} \rho D_s \) [m\(^2\)/s].

For the special case where the sorbed mobile phase is omitted in the model framework, we have \( k_{d1} = 0, D_e = D_c \) and \( \Omega = \Psi = 1 \). Eqs. (1a) and (2a) are identical to (1) and (2).

2.2 Methodologies for solving the stochastic model

2.2.1 Perturbation approach and spectral method

The method used here to solve the stochastic model is similar to those of Gelhar (1976), Espinoza and Valocchi, (1997) and Li and Zhou, (1997), but differs due to the number of random properties and the governing equations. The main assumptions made to solve the problem are: 1) the stochastic processes are second-order stationary, 2) small perturbations in the Laplace domain. Two methods to represent the autocovariance function of an auxiliary variable \( \beta \) in (9) will be presented in the following sections. One is to use an assumption that the matrix has a constant extension that does not influence the stochastic components of the process (Paper V) (later it is referred to as the simple approximation approach). The other approach is to use a Taylor series expansion of the auxiliary variable \( \beta \) (Paper III) (later it is referred to as the Taylor expansion approach).

If we omit the longitudinal dispersion (e.g. Neretnieks, 1980; Cvetkovic, et al., 1999), surface diffusion and radioactive decay, we can, by using Laplace transforms, write equations (1) to (3) with corresponding initial and boundary conditions (4) to (7) as (Maloszewski and Zuber, 1990)

\[ \frac{\tilde{\beta}}{(p, \xi)} + \tilde{\beta}(p, \xi)\tilde{\kappa} = 0 \]  \hspace{1cm} (9)

where

\[ \tilde{\beta} = \frac{p}{u} - \frac{2\tilde{D}}{\tilde{h}} \tilde{\alpha} \left( 1 - \frac{2}{1 + \exp(-2\tilde{\alpha}L)} \right) \]  \hspace{1cm} (10)

\[ \tilde{\alpha} = \sqrt{\frac{p \left( 1 + \tilde{K}_D \frac{k_y}{p + k_y} \right)}{\tilde{D} / \tilde{e}}} \]  \hspace{1cm} (11)

An arbitrary stochastic variable, \( \tilde{x} \), can be expressed as a sum of its expected value (denoted \( E[\ldots] \)) and a perturbation (denoted \( \tilde{\ldots} \)) around the mean:
\[ \tilde{\pi} = E[\pi] + \pi' \] (12)

The expected value of \( \pi' \) is zero, i.e., \( E[\pi'] = 0 \). Introducing the perturbation properties of \( \tilde{c} \) and \( \tilde{\beta} \) into (9), we get

\[ \frac{\partial E[\tilde{c}]}{\partial \xi} + \frac{\partial E[\tilde{\beta}]}{\partial \xi} + E[\beta']E[\tilde{c}] + E[\beta']E[\tilde{\beta}] + \beta' \tilde{c}' = 0 \] (13)

The expected value of (13) (ensemble average) is

\[ \frac{\partial E[\tilde{c}]}{\partial \xi} + E[\beta']E[\tilde{c}] + E[\beta']E[\tilde{\beta}] = 0 \] (14)

where \( s \) is the separation distance between the locations along the x-direction of \( \beta' \) and \( \tilde{c}' \). Expressing the cross-covariance between \( \beta' \) and \( \tilde{c}' \) (for \( s=0 \)) is known as the 'closure problem'.

Subtracting (14) from (13) and assuming small perturbations, i.e., \( \beta' \tilde{c}' - E[\beta' \tilde{c}'] = 0 \) (Espinoza and Valocci, 1997) we get the perturbation equation

\[ \frac{\partial E[\tilde{c}]}{\partial \xi} + E[\beta]E[\tilde{c}] + E[\beta'] = 0 \] (15)

If a random process, \( \beta'(\xi) \), is second order stationary, the spectral density of \( \beta' \) is the Fourier transform of its auto-covariance function (e.g. Marsily, 1986; Vanmarcke, 1988):

\[ \phi_{\beta'}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega s} \text{Cov}[\beta'(\xi)\beta'(\xi + s)]ds \] (16)

where \( \text{Cov}[\ldots] \) denotes the co-variance operator and the stochastic variable \( \beta' \) is defined in terms of a Fourier-Stiltjes integral

\[ \beta'(\xi) = \int_{-\infty}^{\infty} e^{i\omega s} Z_{\beta'}(d\omega) \] (17)

where \( Z \) is a complex stochastic amplitude with zero mean value given as a function of a small increment of the angular frequency, \( d\omega \). The expectation over the total frequency domain divided by \( d\omega \) is the spectral density function defined in (16):

\[ \phi_{\beta'}(\omega) = \frac{E[Z_{\beta'}(d\omega)Z_{\beta'}^{*}(d\omega)]}{d\omega} \] (18)

where the asterisk denotes the complex conjugate and \( E[\ldots] \) denotes the ensemble average also here. Similarly, the cross-spectral density function is defined as
\[
\varphi_{\varepsilon\beta}'(\omega) = \frac{E[Z_\varepsilon'(d\omega)Z_\beta'(d\omega)]}{d\omega}
\]  
(19)

If the stochastic processes in (15) are represented in terms of Fourier-Stiltjes integrals and (19) is used, the cross-spectrum density function of \( \beta' \) and \( \varepsilon' \) becomes

\[
\varphi_{\varepsilon\beta}'(\omega) = -\frac{E[\varepsilon]}{E[\beta] + i\omega} \varphi_\beta'(\omega)
\]  
(20)

Finally, the cross covariance of \( \beta' \) and \( \varepsilon' \) is obtained by Fourier inversion of (20) according to (16):

\[
\text{Cov}[\beta'\xi + s\varepsilon'\xi] = F^{-1}\left[-\frac{E[\varepsilon]}{E[\beta] + i\omega}\right] * F^{-1}[\varphi_\beta']
\]  
(21)

where \( F^{-1}[\ldots] \) denotes the Fourier inversion and \( * \) is the convolution operator. Until now we have got as far as we can get to obtain the 'closure term' in (14) without empirical information. To solve (21) we need information about the auto-covariance of \( \beta \). Since \( \beta \) is a lumped variable that consists of various stochastic variables, two alternatives to represent the auto-covariance of \( \beta \) are presented here.

### 2.2.2 The simple approximation approach

The first alternative, the simple approximation approach, is to assume that the stochastic components of the variables in (1) – (3) can be represented on the assumption that the matrix is effectively infinite and \( k_r \to \infty \) i.e., \( k_r/(p_k) \approx 1 \). The problem thus involves two typical stochastic variables: \( \eta_u = u \tilde{u}, \eta_{Mh} = (Mh)\tilde{(Mh)} \). The variable \( \tilde{M} = \tilde{D}^{0.5}(\tilde{\varepsilon}^{0.5}(1 + \tilde{K}_p)^{0.5}) \) is an ‘effective’ matrix property. Once these stochastic properties have been introduced, the limitation of the permissible depth of the matrix definition is acknowledged. Thus, \( \beta \) can be written as

\[
\tilde{\beta} = c_1 \eta_u + c_2 \eta_u \eta_{Mh}
\]  
(22)

where

\[
c_1 = p/u
\]  
(23)

\[
c_2 = -2D_{hu} \alpha \left| 1 - \frac{2}{1 + \exp(-2L\alpha)} \right|
\]  
(24)

As regards the perturbations, \( \eta = E[\eta] + \eta' \) and \( \beta = E[\beta] + \beta' \), we have

\[
\tilde{\beta} = E[\eta_u]\tilde{1} + E[\eta_u]E[\eta_{Mh}]\tilde{2} + c_1 \eta_{Mh}' + E[\eta_{Mh}]\tilde{2} \eta_u' + E[\eta_u]\tilde{2} \eta_{Mh}' + c_2 \eta_u' \eta_{Mh}'
\]  
(25)
Hence,
\[ E[\beta] = E[\eta]F_1 + E[\eta]E[\eta_{x\eta}]F_2 + C_2 E[\eta, \eta_{x\eta}] \]  
(26)
\[ \beta' = (c_1 + E[\eta_{x\eta}]F_2)\eta' + E[\eta_{x\eta}]F_2 \eta'_{x\eta} + C_2 \eta'_{x\eta} - E[\eta, \eta_{x\eta}] \]  
(27)

Consequently,
\[ \text{Cov}[\beta(x), \beta(x + s)] = E[(\beta - E[\beta])(\beta - E[\beta])_{x+s}] = (c_1 + E[\eta_{x\eta}]F_2)^2 E[\eta(x)\eta'(x + s)] 
+ E^2[\eta_{x\eta}]^2 E[\eta'_{x\eta}(x)\eta'_{x\eta}(x + s)] + C_2 \]  
(28)

Further, the covariance of \( \eta_{x\eta} \) can be expressed in the same way as (28), we then have
\[ \text{Cov}[h_{x\eta}] = E^2[\tilde{M}/M] \text{Cov}[h/\tilde{h}] + E^2[h/\tilde{h}] \text{Cov}[\tilde{M}/M] + \text{Cov}[\tilde{M}/M] \text{Cov}[h/\tilde{h}] + C_2 \]  
(29)

Auto-covariance functions of the stochastic variables \( h/\tilde{h} \) and \( \tilde{M}/M \) have been determined experimentally. The auto-covariance of \( \eta_u \) is then derived from computer simulations of \( u/\tilde{u} \). Experimental results show that the auto-covariances of \( u/\tilde{u} \), \( h/\tilde{h} \) and \( \tilde{M}/M \) follow exponential functions (details will be given in Section 4.1). If the cross-covariance terms \( C_{1} \) and \( C_{2} \) are omitted, the covariance of \( \beta \) can be expressed as a series of exponential functions with different amplitudes, \( a_i \), and correlation lengths, \( \ell_i \), corresponding to the different rock properties:
\[ \text{Cov}[\beta(\xi), \beta(\xi + s)] = \sum_{i=1}^{n} a_i e^{-\xi/\ell_i} \]  
(30)

where \( a_i \) and \( \ell_i \) are defined in Table 1. Once the auto-covariance of \( \beta \) has been determined, (21) can be solved by means of convolution. The closure term in (14) is thus:
\[ \text{Cov}[\beta'(\xi), \tilde{\beta}'(\xi)]_{x=0} = E[\beta \tilde{\beta}']_{x=0} = -E[\tilde{\xi}] \sum_{i=1}^{n} a_i \frac{\ell_i}{E[\beta]_{x=1} + 1} \]  
(31)

where \( a_i \) and \( \ell_i \) are defined in Table 1.

2.2.3 The Taylor expansion approach

The second alternative, the Taylor expansion approach, is to approximate the auxiliary variable \( \beta \) by using the Taylor series expansion. In this way, the maximum possible diffusion depth \( L \) can also be treated as a stochastic variable. The boundary condition (6) is modified to
Table 1 Definition of correlation length $\ell_i$ and typical parameters $a_i$ and $b_i$.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$a_i$</th>
<th>$b_i$</th>
<th>$\ell_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$(c_1^+ E[\eta_{Mh}])c_2^2$</td>
<td>Var[$u/\tilde{u}$]</td>
<td>$\ell_u$</td>
</tr>
<tr>
<td>2</td>
<td>$(c_2)^2 b_2$</td>
<td>$E^2[\eta_{v}]Var[h/\tilde{h}]$</td>
<td>$\ell_h$</td>
</tr>
<tr>
<td>3</td>
<td>$(c_2)^2 b_3$</td>
<td>$E^2[M/M]Var[h/\tilde{h}]Var[u/\tilde{u}]$</td>
<td>$1/\ell_u + 1/\ell_h$</td>
</tr>
<tr>
<td>4</td>
<td>$(c_2)^2 b_4$</td>
<td>$E^2[\eta_{v}]E^2[h/\tilde{h}]Var[M/M]$</td>
<td>$\ell_M$</td>
</tr>
<tr>
<td>5</td>
<td>$(c_2)^2 b_5$</td>
<td>$E^2[\eta_{v}]Var[M/M]Var[h/\tilde{h}]$</td>
<td>$1/\ell_u + 1/\ell_h$</td>
</tr>
<tr>
<td>6</td>
<td>$(c_2)^2 b_6$</td>
<td>$E^2[M/M]E^2[h/\tilde{h}]Var[M/M]Var[u/\tilde{u}]$</td>
<td>$1/\ell_u + 1/\ell_h + 1/\ell_M$</td>
</tr>
<tr>
<td>7</td>
<td>$(c_2)^2 b_7$</td>
<td>Var[$h/\tilde{h}] Var[u/\tilde{u}] Var[M/M]$</td>
<td>$1/\ell_u + 1/\ell_h + 1/\ell_M$</td>
</tr>
</tbody>
</table>

\[ \frac{\partial \tilde{\chi}_m}{\partial z} |_{z=\tilde{L}} = 0 \] (6a)

where $\tilde{L}$ is the maximum possible diffusion depth [m] for a solute in the rock matrix. Here, $\tilde{L}$ is random in the $\xi$-direction, which means that the matrix depth varies.

The auxiliary variable $\tilde{\beta}(\rho, \xi)$ in (9) is rewritten as

\[ \tilde{\beta} = \frac{\rho}{\tilde{\rho}} - \frac{2\tilde{D}_{\eta}}{h\tilde{u}} \left( 1 - \frac{2}{1 + \exp(-2\alpha \tilde{L})} \right) \] (10a)

The term $1/\left[1 + \exp(-2\alpha \tilde{L})\right]$ is approximated by using the Taylor series expansion around $2\alpha \tilde{L} = 0$:

\[ \frac{1}{1 + \exp(-2\alpha \tilde{L})} \approx \frac{1}{2} + \frac{1}{2} \tilde{\alpha} \tilde{L} - \frac{1}{6} \tilde{\alpha}^3 \tilde{L}^3 + \frac{1}{15} \tilde{\alpha}^5 \tilde{L}^5 \] (32)

Only the first four terms in the Taylor series are retained here in the approximation, because this will lead to an exact solution up to the second temporal moments of (9) (the derivation is given in Section 2.4). The approximation of $\tilde{\beta}$ is expressed as

\[ \tilde{\beta} = \frac{\rho}{\tilde{\rho}} + \frac{2\tilde{D}_{\eta}}{h\tilde{u}} \tilde{\alpha} \tilde{L} - \frac{2}{3} \tilde{D}_{\eta} \tilde{\alpha}^3 \tilde{L}^3 + \frac{4}{15} \tilde{D}_{\eta} \tilde{\alpha}^5 \tilde{L}^5 \] (33)

As previously, (33) can be written as
\[ \tilde{\beta} = \beta_1 \eta_u + \beta_2 \eta_{ah} \eta_{M_{l_1}} + \beta_3 \eta_{ah} \eta_{M_{l_2}} + \beta_4 \eta_{ah} \eta_{M_{l_3}} \]  

where \( \beta_1 = \frac{p}{u} \), \( \beta_2 = \frac{2e}{hu} \left[ p \left( 1 + K_D \frac{k_s}{p + k_r} \right) \right] L \), \( \beta_3 = -\frac{2e^2}{3huD_e} \left[ p \left( 1 + K_D \frac{k_s}{p + k_r} \right) \right]^2 L^3 \), \( \beta_4 = \frac{4e^3}{15} \frac{1}{huD_e^2} \left[ p \left( 1 + K_D \frac{k_s}{p + k_r} \right) \right]^3 L^5 \), \( \eta_u = \frac{u}{u} \), \( \eta_{ah} = \frac{u}{u} \cdot h \). By assuming \( k_r \to \infty \), \( \frac{k_s}{p + k_r} \approx 1 \), we get

\[ \eta_{M_{l_1}} = \frac{\tilde{M}_1}{M_1} \frac{\tilde{L}}{L} = \frac{\tilde{\varepsilon}}{\varepsilon} \frac{(1 + \tilde{K}_D)}{(1 + K_D)} \frac{\tilde{L}}{\tilde{L}} \], \[ \eta_{M_{l_2}} = \frac{\tilde{M}_2}{M_2} \frac{\tilde{L}}{L} = \frac{\tilde{\varepsilon}^2}{\varepsilon^2} \frac{(1 + \tilde{K}_D)}{(1 + K_D)} \frac{\tilde{L}}{\tilde{L}} \] and

\[ \frac{\tilde{M}_3}{M_3} = \frac{\tilde{\varepsilon}^3}{\varepsilon^3} \frac{(1 + \tilde{K}_D)}{(1 + K_D)} \frac{\tilde{L}}{\tilde{L}} \].

Following the same procedure as previously, the auto-covariance of \( \beta \) can be expressed as a series of exponential functions as (30) but with 39 terms even if the cross-covariance terms \( CC_1 \) and \( CC_2 \) are omitted. However, only 15 terms effectively contribute to the H-parameters, which are given in Table A-1 (Appendix A). The closure term can then be obtained by means of convolution.

### 2.3 Solutions of one-dimensional solute transport in fractured bedrock

This section presents the solutions of the stochastic model based on the auto-covariance function of \( \beta \) derived by using the simple approximation approach. The solutions derived by using the Taylor expansion approach can be found in Paper III.

When the 'closure term' (31) is determined, the mean concentration in (14) can be solved in the Laplace domain by means of one of the boundary conditions (4):

\[ \mathcal{E}[\tilde{c}] = \frac{M_0}{Q} \exp \left[ -\mathcal{E}[\tilde{c}] + \sum_{i=1}^{q} a_i \left( \mathcal{E}[\tilde{\beta}] \xi_i \right) \right] \]  

(35)

However, the closed form solution in the Laplace domain cannot be inverted to the real time domain to the best of the author's knowledge. Instead, the solute transport is characterised by the temporal moments of the residence time PDF such as the mean and the variance of the residence times in the fracture (see Fig. 4). These properties have been appointed as relevant performance indices by Cvetkovic and Selroos (1999).

The \( k^{th} \) temporal moment of \( f(t) \) is related to the \( k^{th} \) partial derivative of \( L[f(t)] \) with respect to \( p \), evaluated at \( p=0 \):
Figure 4 Principal sketch showing how a breakthrough is characterised by the expected value and the variance of the breakthrough (residence time probability density function).

\[ n_k = \int_{0}^{\infty} f(t, \tau) dt = (-1)^k \frac{\partial^k}{\partial \phi^k} L[f(t, \tau)] \bigg|_{\phi=0} \]

(36)

where \( L[\ldots] \) is the Laplace transform operator, \( p \) is an arbitrary integer defined by the Laplace transform and \( f(t) \) is a PDF for the concentration with the time defined as \( c(\xi, t)/m_0 \), in which \( m_0 = \int_{0}^{\infty} c(\xi, t) dt \). Thus, the central temporal moments are obtained from the well-known relationships as

\[ \mu_t = n_1 \]

(37)

\[ \sigma_t^2 = n_2 - \mu_t^2 = n_2 - n_1^2 \]

(38)

\[ S_t = n_3 - 3\sigma_t^2\mu_t - \mu_t^3 \]

(39)

where \( \mu \) is the expected value \([s]\), \( \sigma^2 \) is the variance \([s^2]\) and \( S \) is the skewness \([s^3]\).

Applying (36) to (35) involves a series of tedious but straightforward operations, which lead to the following expressions for the central temporal moments according to (37) - (39):

\[ \mu_t = \frac{\xi}{u} E[\eta_u] (1 + E[\eta_{th}]) R \]

(40)

\[ \sigma_t^2 = \frac{2}{3} \frac{\xi}{u} R T E[\eta_u] E[\eta_{th}] \left[ 1 + \Psi_1 + 3R \left( \frac{(1+R)^2}{R^2} E[\eta_{th}] H_1 + \sum_{i=2}^{7} H_i \right) \right] \]

(41)
\[ S_t = \frac{4}{5} \varepsilon E[\eta_a] E[\eta_{mb}] R T^2 \left[ 1 + \Psi_1 \Psi_2 + \right. \\
\left. + \frac{5}{2} H_i \frac{1}{R} \left( 3 \frac{H_i}{b_i} E^2 [\eta_a] E[\eta_{mb}] (1 + E[\eta_{mb}] R)^2 + 2 E[\eta_{mb}] R + 2 E[\eta_{mb}] R \Psi_1 \right) \right] + \\
\left. + \frac{5}{2} \sum_{i=2}^{14} \left( H_i \left( 3 \frac{H_i}{b_i} E^2 [\eta_a] E[\eta_{mb}] (1 + E[\eta_{mb}] R)^2 + 2 R + 2 R \Psi_1 \right) \right) \right] 
\]

where the typical numbers, all of which are expected values, are defined in Table 2. The R-parameter is a retardation factor. The T-parameter is a typical residence time for solute transport in the rock matrix. The \( \Psi \)-parameters reflect the kinetics of the sorption process and can be disregarded in the case of equilibrium sorption (\( \Psi_1 << 1 \)). The H-terms reflect the uncertainty relating to heterogeneity of the rock properties. In the case where \( H_i = 0; i = 1,2...7 \) the uncertainty in the effect of parameter variability does not make any contribution to the solution. This case also reflects one single realisation of the heterogeneous rock properties and the single realisation gives a complete representation of the properties. The expected values of \( E[\eta_a] \) and \( E[\eta_{mb}] \) in this case nevertheless represent the effect on the solution of the transport.

**Table 2** Definition of typical parameters governing the propagation of a solute pulse in a fracture.

\[
R = \frac{2 L \varepsilon}{h} (1 + K_D) \\
T = \frac{\varepsilon L^2}{\varepsilon_t D_p} (1 + K_D) \\
\Psi_1 = \frac{3 K_D}{T k_r (1 + K_D)} \\
\Psi_2 = \frac{K_D}{3(1 + K_D)} + \frac{1}{2 T k_r} + \frac{1}{3(1 + K_D)} \\
H_i = \frac{\ell_i b_i}{E[\eta_a] E[\eta_{mb}] u T}
\]

where \( \ell_i \) and \( b_i \) are defined in Table 1.

### 2.4 Comparison of the two approaches for solving the stochastic model

In the previous sections, the solutions of temporal moments of the residence time PDF were derived based on the auto-covariance functions represented by using the simple approximation and the Taylor expansion approaches. This section focuses on comparing the solutions obtained from the two approaches. To do this, \( L \) should not be treated as a random variable. The matrix extension is recognised, however, in the representation of the stochastic components of the other rock properties (as distinct from the simple approximation approach). The problem is thus defined by (9), (10) and (11) with the initial and boundary conditions (4) to (7). Approximating the term \( \sqrt{1 + \exp(-2 \tilde{\alpha}_t)} \) in \( \beta \) by the following expression using Taylor series expansion around \( 2 \tilde{\alpha}_t = 0 \) with the first four terms gives:
\[ \frac{1}{1 + \exp(-2\tilde{\alpha}L)} = \frac{1}{2} + \frac{1}{2} \tilde{\alpha}L - \frac{1}{6} \tilde{\alpha}^2 L^2 + \frac{1}{15} \tilde{\alpha}^3 L^3 \]  

(43)

Thus, \( \beta \) can be expressed as

\[ \tilde{\beta} = \frac{p}{u} + \frac{2\tilde{D}e}{\tilde{h}u} \tilde{\alpha}^2 L - \frac{2}{3} \frac{\tilde{D}e}{\tilde{h}u} \tilde{\alpha}^4 L^3 + \frac{4}{15} \frac{\tilde{D}e}{\tilde{h}u} \tilde{\alpha}^6 L^5 \]  

(44)

In the same way as previously, (44) can be written as

\[ \tilde{\beta} = d_1 \eta_u + d_2 \eta_u \eta_{M,h} + d_3 \eta_u \eta_{M,h} + d_4 \eta_u \eta_{M,h} \]  

(45)

where \( \eta_u \) and \( d_1 \) to \( d_4 \) have the same definitions as in Section 2.2, \( \eta_{M,h} = \frac{\tilde{M}_h}{M_h} \), \( \eta_{M,h} = \frac{\tilde{M}_h}{M_h} \) and \( \eta_{M,h} = \frac{\tilde{M}_h}{M_h} \) where \( \tilde{M}_1, \tilde{M}_2 \) and \( \tilde{M}_3 \) also have the same definition as in Section 2.2.

Following the same procedures as (25) to (29), the auto-covariance of \( \beta \) can be expressed in the same way as (30) but with 15 terms which are defined in Table A-2 (Appendix A). Solving the closure term by means of solving in closed form the convolution operation and substituting it into (14) and using the boundary condition (4) yields:

\[ E[\tilde{\xi}] = \frac{M_0}{Q} \exp \left[ -E[\beta] + \sum_{i=1}^{15} a_i \frac{\ell_i}{E[\beta] + 1} \right] \tilde{\xi} \]  

(46)

where \( a_i \) and \( \ell_i \) are defined in Table A-2 (Appendix A). Applying (36) to (46) and assuming \( E[\eta] = 1 \) we get the central temporal moments:

\[ \mu_r = \frac{\tilde{\xi}}{u} (1 + R) \]  

(47)

\[ \sigma_r^2 = \frac{2}{3} \frac{\tilde{\xi}}{u} R T \left[ 1 + 3 R \left( \frac{1 + R}{R^2} H_1 + \sum_{i=2}^{7} H_i \right) \right] \]  

(48)

When comparing (47) and (48) with (40) and (41) we can see that the results are on the same form for the two approaches, when the expected values of both \( \eta = 1 \). An interesting result is that only 7 terms effectively contribute to the H-parameters although there are 15 terms in (46). It can be shown that if only the first two terms in (44) are used to approximate \( \tilde{\beta} \) the first central moment is the same as (47) but not the second central moment. This is also the reason why the four terms have to be adopted for the approximation of \( \tilde{\beta} \) in the Taylor expansion approach in order to get a correct form of the second temporal moments. From the comparison, we may conclude that the assumption made in the simple approximation approach does not affect the
solutions. However, in some practical cases a slight difference may occur between the two approaches due to the different definitions of the expected $\eta$-values.

2.5 Coupling of mass transfer and flow in a two-dimensional heterogeneous rock fracture

By using a Lagrangian method of description, we can decompose a two-dimensional transport problem into a one-dimensional mass transfer problem and a two-dimensional flow problem (Dagan, et al., 1992, Cvetkovic et al., 1999). The aperture of individual fractures in natural crystalline rock generally varies significantly from practically closed zones to zones with local cavities. Fluid flow in a fracture with variable aperture is commonly described on the basis of Poiseuille law (Moreno et al., 1988, Tsang and Tsang, 1989, Dverstorp et al., 1992 and Cvetkovic et al., 1999, among others). The fluid flow follows

$$
\frac{\partial}{\partial x} \left( h'(x,y) \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left( h'(x,y) \frac{\partial p}{\partial y} \right) = 0
$$

(49)

where $p$ is the pressure [Pa], $h$ is the fracture apertures [m], and $x$ and $y$ are the Cartesian co-ordinates. The flow velocity vector in the fracture is given by

$$
v = -\frac{1}{12\mu} h^2 \nabla p
$$

where $\mu$ is the dynamic viscosity. The streamline field is then computed by tracking a large number of inert particles travelling in the velocity field. The travel time probability density function (PDF) for a large number of particles arriving at the downstream boundary of the fracture is defined as $g(\tau)$, where $\tau$ is the travel time, $\tau = \xi/u$. By means of Monte Carlo simulations we can obtain the expected value of the travel time PDF for inert particles over an ensemble of fractures, $E[g(\tau)]$.

In addition, the PDF of the residence time of solutes in the parcel is denoted $f(t,\tau)$. The expected residence time PDF for the whole distribution of trajectories in a single two-dimensional fracture can thus be obtained as the following (single) fracture average at the downstream control section (Dagan, 1989; Rodriguez-Iturbe and Rinaldo, 1997):

$$
< f(t) >= \int f(t,\tau) g(\tau) d\tau
$$

(50)

Hence, the expected variance of $<\sigma_t^2>$ according to (37) is given as

$$
<\sigma_t^2> = <n_2> - <n_1>^2
$$

$$
= \int_{0}^{\infty} (n_2 - n_1^2) \sigma_t g(\tau) d\tau
$$

$$
+ \int_{0}^{\infty} n_1^2 g(\tau) d\tau - \left( \int_{0}^{\infty} n_1 g(\tau) d\tau \right)^2
$$

(51)

Further, the expected variance of an ensemble of fractures is defined as

$$
E[<\sigma_t^2>] = E\left[ \int_0^{\infty} \sigma_t^2 g(\tau) d\tau \right] + E[\beta]
$$

(52)
If the cross-covariance between the temporal moments for the mass transport along the trajectory paths and $g(\tau)$ is negligible, the first term on the right-hand side of (52) can be written as

$$E \left[ \int_0^\infty \sigma_t^2 g(\tau) d\tau \right] \approx \int_0^\infty E[\sigma_t^2] E[g(\tau)] d\tau \quad (53)$$

Similarly, the second term on the right-hand side of (52) becomes

$$E[\beta] \approx \int_0^\infty E[n_1^2] E[g(\tau)] d\tau - \left( \int_0^\infty E[n_1] E[g(\tau)] d\tau \right)^2 \quad (54)$$

Hence, the relative effect of parameter heterogeneity, $r_{\text{Var}}$, can be defined and rewritten as

$$r_{\text{Var}} = \frac{E[\sigma_t]}{E[\sigma_t(\Delta \sigma_t = 0)]} \approx \frac{1 + \zeta_1}{\zeta_1 + \zeta_2} + \frac{E[\Delta \sigma_t]}{\zeta_1 + \zeta_2} \quad (55)$$

where

$$\zeta_1 = \frac{E[\beta]}{\int_0^\infty E[\sigma_t^2] E[g(\tau)] d\tau} \quad \text{and} \quad \zeta_2 = \frac{\int_0^\infty E[\sigma_t^2(\Delta \sigma_t = 0)] E[g(\tau)] d\tau}{\int_0^\infty 1 + E[\Delta \sigma_t] E[g(\tau)] d\tau}$$

$\zeta_1$ and $\zeta_2$ are two functions representing the heterogeneity of the flow field. In those cases where we have homogeneous flow, $\zeta_1 = 0$ and $\zeta_2 = 1$. 


3. Materials and experimental methods

3.1 Materials

In total, nine drill cores were taken from the Äspö Hard Rock Laboratory, Kalmar County, Sweden. There are two rock types. One is Äspö diorite and the other is Småland granite. Two thin sections from each type of the drill cores were prepared and studied in transmissive light. The average mineral compositions were determined by point counting on the thin sections (Table 3). The dominating minerals of Äspö diorite are plagioclase, potassium feldspar, quartz and biotite. The main minerals of Småland granite are quartz, potassium feldspar, muscovite and saussuritised feldspar. There are a few scattered macropores that presumably have resulted from the dissolution of Fe-Ti oxides. Two drill cores with a diameter of 20 cm and a length of 50 to 60 cm were used in the laboratory bath tests to investigate parameter variabilities. The other seven drill cores with a diameter of 20 cm and a length of 60 to 90 cm were used in the laboratory migration experiments, in which one drill core has a natural fracture.

Table 3 Composition of minerals in Äspö diorite and Småland granite

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Äspö diorite (%)</th>
<th>Småland granite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>20.73</td>
<td>40.99</td>
</tr>
<tr>
<td>Potassium feldspar</td>
<td>16.34</td>
<td>22.96</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>21.71</td>
<td>17.04</td>
</tr>
<tr>
<td>Muscovite</td>
<td>0.24</td>
<td>0.25</td>
</tr>
<tr>
<td>Biotite</td>
<td>13.17</td>
<td>2.72</td>
</tr>
<tr>
<td>Hornblende</td>
<td>6.34</td>
<td>-</td>
</tr>
<tr>
<td>Fe-Ti oxides</td>
<td>0.98</td>
<td>0.25</td>
</tr>
<tr>
<td>Titanite</td>
<td>1.95</td>
<td>1.48</td>
</tr>
<tr>
<td>Saussuritized feldspar</td>
<td>15.85</td>
<td>12.84</td>
</tr>
<tr>
<td>Others*</td>
<td>2.68</td>
<td>1.48</td>
</tr>
<tr>
<td>Total number of grains counted</td>
<td>411</td>
<td>406</td>
</tr>
</tbody>
</table>

*Others include zircon, calcite, epidote and chlorite.

3.2 Geostatistical analysis and batch test planning

As mentioned earlier, two drill cores in each series were used to determine the adsorption characteristics, the porosity and the effective diffusivity. A large number of samples were taken to obtain a sufficient statistical significance of the data. Table 4 summarises the experiments included in the study.

Rock slabs were taken in a certain pattern (see Fig. 5) which facilitated a reliable geostatistical analysis of the data in two dimensions. The size of each slab face was 20x20 mm and the thickness varied in the range 6 - 15 mm.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Åspö diorite slab thickness</th>
<th>Småland granite slab thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (leaching method, NaI)</td>
<td>4 mm, &gt; 50 samples</td>
<td>6 mm, &gt; 50 samples</td>
</tr>
<tr>
<td></td>
<td>6 mm, &gt; 50 samples</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10 mm, &gt; 50 samples</td>
<td>10 mm, &gt; 50 samples</td>
</tr>
<tr>
<td></td>
<td>15 mm, 10 samples</td>
<td></td>
</tr>
<tr>
<td>$D_e$, effective diffusivity (through-diffusion, NaI)</td>
<td>4 mm, &gt; 50 samples</td>
<td>6 mm, &gt; 50 samples</td>
</tr>
<tr>
<td>(through-diffusion, NaI)</td>
<td>6 mm, &gt; 50 samples</td>
<td></td>
</tr>
<tr>
<td>$k_d$, partition coefficient (in-diffusion method)</td>
<td>10 mm, 12 samples particle size: 0.0065, 0.011, 0.0154, 0.0227, 0.104, 0.65, 1.198 and 2.397 mm*</td>
<td>10 mm, 3 samples</td>
</tr>
<tr>
<td>(crushed particles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Migration experiment</td>
<td>3 sets</td>
<td>3 sets</td>
</tr>
</tbody>
</table>

The auto-covariance function or semi-variogram of the measured data can be estimated by taking the samples in a suitable pattern in which there are certain separation distances between the samples. The correlation length in an arbitrary direction in the $(x, y)$-plane, $\ell$, was evaluated based on the assumption of isotropic conditions.

### 3.3 Porosity measurements

The porosity of the samples was measured by means of the leaching method (Skagius and Neretnieks, 1986). The rock slabs were placed in a vacuum chamber to remove gas trapped in pores and then saturated with a solution of iodide with a concentration of 1.25 M for at least three weeks. The amount of iodide in each slab in the saturated condition was determined by placing the iodide-saturated sample in distilled water and measuring the leaching of iodide from the slabs. The leaching was performed until the iodide concentration of each solution became practically constant with time. The experiments show that the equilibrium is reached after a period of at least three weeks. The pore volume and the porosity of the slab were then calculated by means of a formulation of the mass balance of iodide.

### 3.4 Effective diffusivity measurements

The effective diffusivity was determined with the through-diffusion technique described by, for example, Johansson et al. (1997). The apparatus for a through-diffusion experiment is shown schematically in Fig. 6. The rock slab was placed in a quadratic hole being fixed to a PVC plate with silicone rubber. The plate with the rock slab was then kept in a vacuum chamber for air removal and saturated with distilled water in the same way as in the porosity measurements. After saturation, the plate was...
mounted between two water containers and sealed with O-rings on both sides. The volume of the containers was 20 mL. One side of the diffusion cell was filled with 0.1 M sodium iodide solution as a tracer substance. The other cell was filled with 0.1 M sodium nitrate solution in order to avoid osmotic effects (Skagius and Neretnieks, 1986). Samples (1 mL) were repeatedly taken from the cell with sodium nitrate. Each time a sample was withdrawn, 1 ml of sodium nitrate solution was added to the cell to maintain a constant liquid volume in the cell. The sodium iodide concentration in the samples was measured by an iodide selective electrode (AST Orion Model 9653).

![Diagram of the diffusion cell](image)

**Fig. 5** Schematic of the disintegration of a drill core and the pattern of a rock slab sampling. Black squares represent slabs to be investigated with regard to a specific parameter.

![Diagram of the diffusion cell](image)

**Fig. 6** Schematic of the diffusion cell (design after Johansson et al. 1997). A tracer container. B O-ring, C rock sample, D PVC plate, E sampling hole and rubber plug, F measurement container, G silicone rubber.
The measured sodium iodide concentrations were evaluated by means of the diffusion theory described by Skagius and Neretnieks (1986). The total amount of diffusing substance, $Q_T$, passing through the slab during the time $t$ can be obtained by solving the diffusion equation for the following boundary conditions: the concentration, $C_1$, on the upper side of the slab, at $x=0$, is constant for $t \geq 0$ and the concentration, $C_2$, on the lower side of the slab, at $x=l$, is much less than $C_1$ for $t \geq 0$, where $l$ is the thickness of the slab. If $C_2 = 0$, the solution to the diffusion equation with constant parameters becomes

$$Q_T = C_1 D_e l - C_1 \frac{\kappa l^6}{6} - 2\kappa C_1 l \sum_{n=1}^{\infty} \frac{(-n)^n}{n^2} \exp \left( -\frac{D_e n^2 \pi}{l^2 \kappa} \right)$$  \hspace{1cm} (56)

where $\kappa$ is the adsorption capacity of the rock in the form of $\varepsilon + K_D \rho$ and other variables have the same definition in Section 2.1. As $t$ tends to $\infty$, (56) takes the form of

$$Q_T = C_1 D_e l - C_1 \frac{\kappa l^6}{6}$$  \hspace{1cm} (57)

The assumptions underlying (57) are that $D_e$ is constant, the concentration in the injection cell $C_1$ is constant with time, the concentration in the measuring cell $C_2$ is negligible compared to $C_1$ for all times, and the slab is homogeneous in its thickness and quasi-steady state is reached (time derivatives tend to zero as the time tends to infinity). These assumptions should be reasonable for the through-diffusion experiments. The effective diffusivity $D_e$ will be obtained by fitting the measured data to (57).

### 3.5 Method for determining adsorption kinetics on crushed rock particles

Batch tests with crushed rock have been conducted to determine the sorption rate coefficient valid when the kinetics is governed predominantly by rate-limited processes at the solid surface, and not by diffusion in micro-fissures of the rock material. Therefore, an important part of the evaluation is to select those grain size fractions in which the surface area of the grains dominate the total area available to sorption. The particle surface area can be defined as the 1) the external geometric surface area, $A_E$, including surface roughness, 2) the physical surface area, $A_T$, including the internal surface area, $A_{IN}$, of (micro) pores and/or (micro) fissures and external geometric surface area $A_E$, and 3) the geometric surface area of a sphere with the same diameter as that of the mean particle (surface area of the equivalent sphere), $A_{ES}$. Fig. 7 schematically represents the three surface concepts.

Particles were produced from Åspö diorite collected in the form of drill cores at Åspö Hard Rock Laboratory. The total (physical) surface area, $A_T = A_E + A_{IN}$, was measured for three particle size fractions (mean diameters by volume were 0.0154, 0.605 and 1.198 mm) using nitrogen gas and Micromeritics Flow Sorb II (i.e. the BET surface area). The results were evaluated assuming that the internal surface area is
proportional to the cube of the particle diameter (volume of particle) and the external area is proportional to the square of the particle diameter. These assumptions lead to the following expression for the surface factor:

$$\lambda_g = \frac{A_T}{A_{ES}} = a d_{50} + \frac{A_E}{A_{ES}}$$

(58)

where $A_{ES}$ is the surface area of a sphere having equivalent diameter as the particle, $a$ is a constant and subscript 50 denotes the arithmetic mean by volume.

As can be seen in Fig. 8, the $\lambda_g$-value for the smallest particle size, 0.0154 mm, is practically identical to the intercept value $A_E/A_{ES}$, i.e. the surface roughness. Hence, for the smallest particles, (58) gives $A_T \approx A_E$. The intercept is about 7, which is similar to the value reported by Anbeek (1992). In other words, the surface area of the 0.0154 mm particles is dominated by the external surface area. Consequently, only the particles with a size of 0.0154 mm are included in the evaluation of the surface sorption kinetics.

**Fig. 7** Definition of particle surface: 1) external geometric surface area, 2) physical surface area, which includes the internal surfaces of (micro) pores and/or (micro) cracks, and 3) geometric surface area of a sphere with the same size as the mean particle.

**Fig. 8** Particle size, $d_{50}$, versus $\lambda_g$ according to data (stars) and (58) (line).
A 200 mL batch solution was prepared by adding $^{137}\text{Cs}$ in dissolved form into synthetic ground water (Allard and Beall, 1979) and mixed with a suspension of crushed diorite. Samples of about 1 mL were repeatedly withdrawn from the gently shaken batch solution and immediately separated (by centrifugation) into their dissolved and particulate components. The partition ratio between the particulate and the dissolved phase, $k_d$, was obtained by measuring the decrease in the concentration of the clear water phase. The initial concentration of Cs was $1.3 \times 10^{-5}$ M. The particle concentrations were 40 g/L, 60 g/L, 100 g/L and 150 g/L which correspond to the specific surfaces 38,218, 56,842, 93,527 and 137,837 m$^2$/m$^3$. The experiments were performed at room temperature and under oxic conditions.

3.6 Method for determining adsorption kinetics on intact rock

The estimation of adsorption kinetics for intact rock was based on the evaluation of experimental data from the in-diffusion tests using the model described in section 2.1. The in-diffusion technique described by Ittner et al. (1990) was employed. The rock slabs had a size of $2 \times 2 \times 1$ cm and were coated with silicone rubber on all sides except one. The samples were kept in contact with synthetic groundwater for about two months for pre-equilibration before being submerged in the synthetic groundwater with $^{137}\text{Cs}$ as tracer element. Hence, the Cs ions start to slowly diffuse into the only open side of the rock slab which gives rise to a concentration profile with depth in the rock.

After a contact time of more than 6 months, the slab was taken out from the solution and washed. Layers 0.1 mm thick were successively removed from the slab using sandpaper. The trace element was analysed by measuring the radioactivity of the removed material, including the sandpaper. The radioactivity was measured with a $\gamma$-counter (CG-4000).

The rate of diffusion of $^{137}\text{Cs}$ through the slab follows the same mathematical framework as outlined in Section 2.1, particularly (1a), (2a) and (3). However, all the stochastic variables are treated as mean values in the evaluation of the in-diffusion experiments. The free water phase (corresponding to the main fracture) is homogeneous in the in-diffusion experiments, whereby the differential terms in space and radioactive decay can be disregarded in (1a). Further, (1a) should be averaged over the cross-section, $A$ [m$^2$], of the rock sample. The system of equations is solved numerically by means of the central finite difference and the Crank-Nicolsons approximation for time. All the parameters ($\varepsilon$, $\varepsilon_t$, $D_p$ and $\rho$) in the system of equations are determined independently except for $D_s$, $k_t$, $K_D$ and $k_d1$, which are estimated by fitting the solution of the system of equations to the measured concentration profile.

3.7 Laboratory migration experiments

Six drill cores of Äspö diorite (ÅD), denoted ÅD-1, -2 and –3, and Småland granite (SG), denoted SG-1, -2 and -3, each with a diameter of 20 cm and a length of 60 to 90 cm, were used in the migration experiments.
The drill cores were sawn into two parts along the drill cores' axes and the sawn surfaces were polished. The two parts were then assembled together with an artificial fracture aperture of 1 mm between them and the outer surfaces were sealed with silicone rubber. The flow rate was controlled by using a gravity feed system similar to that of Wels et al., (1996). To reduce hydrodynamic dispersion, the inlet and outlet were connected via five triangular slits to the fracture. Further, the slits were connected to five outlet tubes, each with a diameter of 0.3 mm and a length of 1 m, which provides sufficient resistance to obtain the desired flow rates. The tracer was injected by switching the valve opening from the water container to the tracer container. The outflow was collected with a fraction collector which was set to collect one hour's sample per bottle. The sample drops were collected in bottles with QUICKSAFE-A scintillation liquid (Zinsser analytic). The $^3$H$_2$O content was analysed with an ISOCAP/300 beta-scintillation counter. The flow rate was monitored by weighing each collected sample.

The initial concentration of $^3$H$_2$O was 2,500 Bq/mL. Migration experiments with glass fracture were performed to estimate the effect of the hydrodynamic dispersion of the fracture set-up. Table 5 summarises the details of the experiments.

Table 5 Experimental conditions in migration experiments with $^3$H$_2$O as tracer.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Length of the drill core (cm)</th>
<th>Velocity (m/min)</th>
<th>Injection duration (hours)</th>
<th>Markers</th>
</tr>
</thead>
<tbody>
<tr>
<td>ÄD-1</td>
<td>78</td>
<td>3.41\times10^{-4}</td>
<td>2</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.43\times10^{-5}</td>
<td>3</td>
<td>*</td>
</tr>
<tr>
<td>ÄD-2</td>
<td>64.5</td>
<td>3.33\times10^{-4}</td>
<td>2</td>
<td>□</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.18\times10^{-4}</td>
<td>3</td>
<td>□</td>
</tr>
<tr>
<td>ÄD-3</td>
<td>60</td>
<td>2.66\times10^{-4}</td>
<td>2</td>
<td>Δ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.10\times10^{-4}</td>
<td>3</td>
<td>Δ</td>
</tr>
<tr>
<td>SG-1</td>
<td>73</td>
<td>7.33\times10^{-5}</td>
<td>2</td>
<td>&lt;</td>
</tr>
<tr>
<td>SG-2</td>
<td>86</td>
<td>2.75\times10^{-4}</td>
<td>2</td>
<td>△</td>
</tr>
<tr>
<td>SG-3</td>
<td>88</td>
<td>3.23\times10^{-4}</td>
<td>2</td>
<td>+</td>
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<td></td>
<td></td>
<td>1.06\times10^{-4}</td>
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<tr>
<td>GL</td>
<td>80</td>
<td>4.91\times10^{-4}</td>
<td>2.5</td>
<td>O</td>
</tr>
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<td></td>
<td></td>
<td>2.21\times10^{-4}</td>
<td>2</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.26\times10^{-4}</td>
<td>3</td>
<td>O</td>
</tr>
</tbody>
</table>
4. Results of experiments and interpretations

4.1 Results of batch experiments (Papers I, II and V)

Table 6 summarises the porosity and diffusivity data. The fact that the porosity decreases with increasing slab thickness is probably caused by stress release resulting from the sawing. The distribution of the porosity is positively skewed for all slab thickness classes, reflecting the fact that a few samples have a markedly high porosity. One rock core of each of ÅD and SG having a diameter of 24 mm and a length of 40 mm were sent to the Laboratory of Radiochemistry at the University of Helsinki for complementary porosity measurements. The porosity was 0.33±0.05% and 0.22±0.03% measured by the $^{14}$C-PMMA method (Hellmuth, et al., 1993) for ÅD and SG samples, respectively. The porosity value measured on 15 mm ÅD slabs by the leaching method is close to that measured by the $^{14}$C-PMMA method. The directional dependence of the auto-covariance is insignificant, which suggests that the measured properties are effectively isotropic.

Results from the in-diffusion experiments were evaluated using the transport model described previously and the optimisation procedure used by Xu and Wörman (1998). There is no distinct optimum, but the procedure results in an upper limit of $k_r$ which is used in the conservative impact analysis of sorption kinetics on radionuclide migration. The following results were obtained as a mean: $k_d = 0.02$ m$^3$/kg, $k_r = 2.72 \times 10^{-8}$ s$^{-1}$. The coefficients of variation of $k_r$ and $k_d$ were 10.8% and 27%, respectively.

On the assumption that the specific inner surface for intact rock is about 100 m$^2$/kg$^{-1}$, that is 270,000 m$^2$/m$^{-3}$, the measured sorption rate coefficient from crushed particles is interpreted for the sorption rate coefficient, $k_r$, for intact rock as $k_r = 4 \times 10^{-6}$ s$^{-1}$, which is 2 to 3 orders of magnitude larger than that obtained for intact rock. The probable

<table>
<thead>
<tr>
<th>Table 6</th>
<th>Summary of porosity and effective diffusivity values obtained in different experiments.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>Mean porosity %</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------</td>
</tr>
<tr>
<td>4 mm ÅD</td>
<td>0.84</td>
</tr>
<tr>
<td>6 mm ÅD</td>
<td>0.70</td>
</tr>
<tr>
<td>10 mm ÅD</td>
<td>0.55</td>
</tr>
<tr>
<td>15 mm ÅD</td>
<td>0.40</td>
</tr>
<tr>
<td>6 mm SG</td>
<td>0.39</td>
</tr>
<tr>
<td>10 mm SG</td>
<td>0.36</td>
</tr>
<tr>
<td>Samples</td>
<td>Mean effective diffusivity $\times 10^{-13}$ m$^2$/s</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>4 mm ÅD</td>
<td>4.45 $\times 10^{-13}$</td>
</tr>
<tr>
<td>6 mm ÅD</td>
<td>8.77 $\times 10^{-13}$</td>
</tr>
<tr>
<td>6 mm SG</td>
<td>1.07 $\times 10^{-13}$</td>
</tr>
</tbody>
</table>
explanation is that the sorption kinetics evaluated for intact rock is primarily due to rate-limited transport in intra-granular micro-fissures, whereas the sorption kinetics for the crushed rock is primarily due to surface processes.

Finally, the auto-covariance functions of the effective matrix parameter, $\tilde{M}/M$, are obtained for diorite samples by evaluating the data from the batch tests mentioned above. The exponential model, $\text{Cov}[\tilde{M}/M] = \text{Var}[\tilde{M}/M] \exp(-s/\ell_M)$, fits the $\tilde{M}/M$ data well, where $s$ denotes the separation distance and $\ell_M$ is the correlation length of $M$ in an arbitrary direction in the $(x, y)$-plane. The correlation length and variance of $\tilde{M}/M$ vary with the exact definition of $M$ (Papers II, III and VI) and experimental series.

4.2 Effect of sorption kinetics on radionuclide migration (Paper I)

Investigations of Cs-adsorption in aquatic sediments indicate that the equilibration times for sorption processes vary from weeks in laboratory tests with illite and montmorillonite (Comans and Hockley, 1992) up to several years or decades under special field conditions for Chernobyl Cs in lake sediments (Meili and Wörman, 1996). The effect of sorption kinetics on the radionuclide migration in fractured rock is studied in order to distinguish this effect from the effect of heterogeneity of rock properties on radionuclides migration. The sorption kinetics of Cs for Åspö diorite was determined by using both crushed rock particles and intact rock slabs. The effect of sorption kinetics on the radionuclide migration in fractured rock is analysed by means of the governing equations of (1a), (2a) and (3) with certain boundary and initial conditions specified by (4) to (8). An exact solution is derived in a form of the temporal variance of a pulse travelling in a fracture.

The two measures appointed in this study are the peak value of the concentration pulse, $P(\xi)$, and the variance of the residence time probability density function, $\sigma_t^2$, (width of the pulse). The relative error in the peak concentration resulting if sorption kinetics is omitted is defined as $\varepsilon_{\text{peak}} = (P_k - P_E)/P_E$, where subscripts $k$ and $E$ denote 'kinetic sorption' and 'equilibrium sorption' (i.e. $k_r \to \infty$), respectively. The relative error of the peak value was analysed numerically using the computational package of Wörman and Xu (1996). The other measure is the relative error of the variances of the residence time PDF, which is in the form of a temporal variance of a pulse travelling in a fracture resulting if sorption kinetics is omitted, namely $\varepsilon_{\text{var}} = (\sigma_{t,k}^2 - \sigma_{t,E}^2)/\sigma_{t,E}^2$, where subscripts $k$ and $E$ have the same definitions as above.

An example simulation was conducted for a pulse of Cs travelling through a rock fracture. The result shows that adsorption kinetics increases the height of the peak in the breakthrough by as much as 31% compared with the equilibrium case (Fig. 9). The reason for this result is that sorption kinetics during the uptake phase can be interpreted as a decrease of the effective partition coefficient. This, in turn, leads to a lowering of the mass retention. In contrast, adsorption kinetics during the release phase can be interpreted as a net increase of the partition coefficient. In other words, sorption kinetics is manifested in terms of a higher peak value and lower tail values.
Equilibrium chemistry

Fig. 9 Breakthrough curve for $\xi k_r/u = 3.5 \times 10^{-3}$, $k_d \rho/\varepsilon = 1.4 \times 10^4$, $D' L/\left(h D_p \varepsilon/\varepsilon\right) = 2 \times 10^{-3}$, and $E k_r/\varepsilon = 4.5 \times 10^{-7}$ due to a Dirac pulse of Cs defined at the upstream boundary.

compared with equilibrium sorption case. The kinetics case has a lower mass retention at maximum but a more prolonged retention effect than the equilibrium case. Hence, after a long time, the tail in the kinetics case will eventually exceed that of the equilibrium case.

A case study was conducted using the reference values of Cs migrating in the bedrock sampled at the Åspö Hard Rock Laboratory. The relative error in the variance of the residence times, resulting from the omission of sorption kinetics is about 10 % for the reference case. The reference case is marked in the contour plot in Fig. 10, which shows the relative error versus $K_D$ and $L^2 k_r/\left(D_p \varepsilon/\varepsilon\right)$. The other parameters kept constant in Fig. 10, are not primary ones. Only a few variables affect $\varepsilon_{var}$. If Cs and Åspö diorite are considered, only L has a significant influence on the relative error according to the solution. A decreasing value of L results in an increasing error. However, the error is higher for less sorbing nuclides than Cs. A maximum error occurs for $K_D = 1$.

4.3 Effect of Taylor dispersion in laboratory migration set-up (Paper VI)

Transverse mixing in combination with transverse velocity gradients is a primary factor in the transport of solutes in both natural environments and engineered systems. The velocity gradients imply a spatial variation of the mass flux, which gives rise to a longitudinal spreading of the solute mass known as shear dispersion (Townsend, 1951
Following the classic assumption of Taylor that the gradients in the longitudinal advection and the transverse mixing are completely balanced in a moving frame of reference, the mathematical formulation is extended to a two-dimensional laminar flow problem. With restrictions that the flow conduit has parallel straight walls and steady-state transport prevails in a moving frame of reference, the coefficient for shear dispersion in the formulation can be expressed as a unique function of the aspect ratio \((H/W)\) of the cross-section. Here, \(H\) denotes the height of the vertical aperture and \(W\) the width. The two-dimensional flow problem in a rectangular flow conduit under steady-state conditions corresponds to the conditions in the tracer experiments in fractured granite drill cores. Numerical simulations are performed with various aspect ratios of the rectangular cross-section. The results show that the closed-form solution, derived on the assumption of infinite width, only applies with an acceptable degree of accuracy only if the aspect ratio is less than about \(10^{-3}\). The maximum deviation occurs at around the aspect ratio of 0.06 by a factor of about 7 (see Fig. 11).
Fig. 11 Variation of $\alpha$ with the aspect ratio for enclosed laminar flow in the range $0.0002 < H/W < 1$, where $\alpha$ is a proportionality coefficient that depends only on the geometry. The dashed line corresponds to the analytical solution, $E = H^2 \langle u^2 \rangle / (210D)$, derived for an infinite width.

4.4 Effect of heterogeneity of rock properties on radionuclide migration

4.4.1 Mass transfer (Papers III and V)

The effect of heterogeneous rock properties on radionuclide migration is analysed by estimating the expected value and variance of the solution of the stochastic transport model for all possible realisations of the rock properties. The most relevant rock properties, including advection velocity, fracture aperture and several matrix properties such as porosity, effective diffusivity and partition coefficient, are assumed to be spatially variable in the direction of the longitudinal transport. The reason for this assumption is that the depth of penetration of solutes in the matrix is much smaller than the correlation lengths characterising the variability of the parameters over the fracture plane. The heterogeneity of both fracture aperture and matrix properties can be substantial in crystalline rock (Hakami and Barton, 1990; Xu and Wörman, 1998). The correlation lengths found for porosity and fracture aperture in these studies were much larger than the depth of penetration expected for radionuclides in a homogeneous rock matrix during the time periods of interest to a safety assessment of nuclear waste repositories in bedrock (Neretnieks, 1980; Neretnieks et al., 1982).
The problem is first solved in a general form by means of a spectral analysis performed in the Laplace domain. Specific one-dimensional solutions to the mean values of the temporal moments of the residence time PDF are then derived for autocovariance functions fitted to data obtained for rock samples taken at Åspö Hard Rock Laboratory. Both the closed-form solutions and numerical Laplace inversions indicate that heterogeneity of the rock properties contributes to increasing both the variance and the skewness of the residence time PDF for a pulse travelling in a fracture.

The analyses can be extended to include one more parameters, the maximum diffusion depth, as a stochastic variable by using a Taylor series expansion of the auxiliary variable $\beta$ in (9). This method leads to a general way to handle the stochastic variables in the governing equations (Paper III). The heterogeneity of the diffusion depth also has a significant effect on the radionuclide migration in fractured rocks. The heterogeneity contributes to an increasing variance of the residence time PDF, which reduces the peak value of a pulse travelling in a fracture.

4.4.2 Heterogeneity of flow field (Paper II)

As shown by the previous one-dimensional analytical solutions to the mean values of the temporal moments of the residence time, PDF has been obtained for the solute transport in a heterogeneous physical and geochemical aquifer. The one-dimensional analyses show that the heterogeneity of the rock properties can have a substantial impact on the transport. A case study of the effect of heterogeneity in matrix diffusion for a single fracture could be performed by decomposing the transport problem into a one-dimensional mass transfer problem and a two-dimensional flow problem using a Lagrangian method of description.

The random spatial aperture fields were generated by an algorithm using the turning bands method (Mantoglou and Wilson, 1981) based on the fracture statistics taken from the findings of Hakami (1995), who used the same rock type as investigated in this study. The stochastic flow fields were obtained by first solving the flow problem (49) and then using a particle tracking technique (Fig. 12). Monte Carlo simulations with 1,000 fracture realisations were used to derive the expected travel time PDF for an ensemble of water parcels arriving at a certain control section. The simulation domain size was $1 \times 1 \text{m}^2$.

Results from Monte Carlo simulations indicate that the expected travel time PDF for inert water parcels in a single fracture in granitic rock becomes increasingly skewed with increasing correlation length of the fracture aperture (Fig. 13). Heterogeneous matrix diffusion along the trajectory paths increases the variance of the travel time PDF of a solute. The impact on the solute transport of the heterogeneous mass transfer with the rock matrix along the trajectory paths is significantly more pronounced than the effect of the macro-dispersion caused by the differentiation of the flow paths. However, upscaling these small-scale transport phenomena investigated in this study into a PA model requires more advanced flow models than that employed in this study, such as a flow model with a network of discs with stochastic radius (Andersson and Dverstorp 1987; Nordqvist et al., 1992 and Dverstorp et al., 1992).
Fig. 12 Trajectory paths in a rectangular fracture, in which the fracture aperture $h=1.2$ mm, $\text{Var}[h] = 0.7$ and the correlation length $\lambda_h = 0.04$ m.

Fig. 13 The expected travel time PDF of an ensemble of water parcels travelling through a fracture with a stochastic aperture characterised by different correlation lengths. The coefficient of variation of the aperture was 0.7.

4.5 Migration experiments (Paper IV)

Laboratory migration experiments were performed with tritium (Fig. 14) so as to obtain results that could be compared with the analytical solutions combined with the auto-covariance functions obtained from the independent laboratory bath tests. Each
migration experiment was performed with a non-sorbing tracer, constant velocity and aperture. Based on (41) the relative impact of taking into account the effect of the heterogeneity of the effective matrix property M can be expressed in the following form

$$\frac{\sigma_t^2}{\sigma_t^2(H_i = 0)} = 1 + 3RH_z = 1 + \frac{6D_e}{h} \frac{\sigma_M^2}{\ell_M} \frac{L u}{h}$$  \hspace{1cm} (59)$$

By systematically varying the flow velocity, u, between different set-ups, we may qualitatively verify the non-linear influence of 1/u on the variance of the residence time PDF. To evaluate the laboratory migration experiments, the temporal moments of the probability density function for the residence time, n_k, can be obtained from the breakthrough curves of the migration experiments according to, for example, Wörman (2000):

$$n_k = \int_0^\infty t^k f(t) dt \hspace{1cm} k=1,2,3\ldots \hspace{1cm} (60)$$

where f(t) has the same definition as in (36). Thus, the central temporal moments can be obtained according (37) - (39).

Fig. 15 shows the variance of the residence time PDF versus the flow velocity obtained from the migration experiments performed in a glass fracture set-up. The dashed line is an approximation function. The variance of the residence time PDF, $\sigma_t^2$,.

Fig. 14 Six drill cores and a glass fracture set-up used in laboratory migration experiments performed with $^3$H as tracer.
caused by the hydrodynamic dispersion is an additive term such as $2x\varepsilon E/u^3$ in the complete solution to $\sigma_t^2$, which includes advection, dispersion, matrix diffusion and kinetic sorption for a non-sorbing tracer pulse travelling in a fracture (Paper I). $E$ denotes the sum of the coefficient of molecular diffusion and hydrodynamic dispersion. Since hydrodynamic dispersion is not included in (40) - (42), the variance caused by the hydrodynamic dispersion (Fig. 15) has been subtracted from the variance measured in the migration experiments with the drill cores before the plot in Fig. 16. In a natural fracture the flow velocity is likely to be smaller than used in the experiments. The effect of shear dispersion can thus be neglected.

Fig. 16 shows the relative effect of the variance ($\sigma_t^2/\sigma_{t(H^3O_\gamma=0)}^2$) simulated according to (59) and the relative variance obtained from the migration experiments with various drill cores versus the inverse of the flow velocity, $1/u$. As can be seen, most of the data follows the dashed line (the theory) in Fig. 16, which suggests that the solutions derived in this study seem to adequately represent the effect of the heterogeneous rock properties on the solute transport. The values used to interpret the experiments are: $h=0.001 \text{ m}, \varepsilon=0.005, \varepsilon_c=0.0036, L=0.0026 \text{ m}, D_c=3\times10^{-13} \text{ m}^2/\text{s}, \sigma_{\tilde{M}M}^2=0.41$ and $\ell_M=0.18 \text{ m}$.

Since tritium is a non-sorbing tracer, $K_D=0$ and $\tilde{M}/M$ simplifies to $(\tilde{D}_p \varepsilon \varepsilon)^{0.5}/(D_p \varepsilon \varepsilon)^{0.5}$. The correlation length of $\tilde{M}/M$ associated with the exponential model was found to lie in the range of $0.05<\ell_M<0.18 \text{ m}$ and the variance of $\tilde{M}/M$ was found to vary in the interval $0.069<\sigma_{\tilde{M}M}^2<0.41$ depending on the experimental series.

![Graph of variance vs. time](image)

*Fig. 15* Variance of the residence time PDF versus $x/u$ obtained from the migration experiments performed in a glass fracture set-up.
Practical limitations and various other factors cause uncertainties in the results. The main causes for such uncertainties are that 1) the data from the two bedrock types (diorite and granite) is combined (in this section) to derive joint statistics of the Åspö granite, 2) only 6 drill cores are used in the migration experiments which leads to a small statistic basis for the evaluation, 3) uncertainty is involved in the evaluation of the variance in each migration experiment.

5. Implication of results for radionuclide transport in granite fractures (Paper V)

The importance of taking into account the uncertainty in heterogeneous rock properties for radionuclide migration was analysed and exemplified for plausible cases of radionuclides migrating from a waste repository in the Swedish granitic bedrock. For this purpose, a sensitivity analysis of the $\sigma_i^2 / \sigma_i^2(H_i = 0)$- and the $S_t/S_t(b_i = \ell_i = 0)$-ratio was performed based on data typical to the Åspö data. To simplify the analysis, the effects of the actual (real) spatial parameter variability along the transport paths were omitted, i.e., all expected values of $\eta$ were assumed to be unity. Further, for most radionuclides in crystalline rock $1 << R$ and assuming an instantaneous sorption process equations, (41) and (42) can be simplified as

$$\frac{\sigma_i^2}{\sigma_i^2(H_i = 0)} \approx 1 + 3R \sum_{i=1}^{7} H_i$$

(61)
Typical geostatistics obtained for the crystalline rock at Åspö Hard Rock Laboratory are given by: \( \ell_M = 0.1 \) m, \( \ell_h = 0.04 \), \( \text{Var}[\tilde{M}/M] = 0.3 \), \( \text{Var}[\tilde{h}/h] \approx \text{Var}[\tilde{h}/h] = 0.7 \). Further, by means of numerical simulation of the flow field in a rock fracture, using the simulation technique described by Wörman and Xu (1996) and the applicable aperture statistics, we were able to calculate a large set (1,000) of stream line fields of the type shown in Fig. 12. Hence, the covariances of the fracture aperture and the advection velocity along the stream lines was found to approximately follow exponential models, in which \( \ell_h = 0.18 \), \( \text{Var}[\tilde{h}/h] = 0.7 \), \( \ell_u = 0.18 \) and \( \text{Var}[\tilde{u}/u] = 0.14 \). The details of these flow simulations can be found in Paper II. Nonetheless, given the statistics accounted for, the sum of \( \ell_i b_i \) was found to be about 0.21 and the sum of \( \ell_i^2 b_i \) about 0.032.

Other parameters that are considered to be constants in the sensitivity analysis are the effective diffusivity, the \( \varepsilon/\varepsilon_t \) ratio and the permissible diffusion depth. These values are specified in the headlinings of Table 7. Variables exhibiting a significant variation in the bedrock are assumed to be the advection velocity and the fracture aperture. The mean values of these variables co-vary, approximately in accordance with a Pouiseuille flow: \( u = 8495 \) J h\(^2\), where \( J \) is the hydraulic gradient.

The theory of Pouiseuille flow is used to interpret the flow measurements of Rasmuson and Neretnieks (1986) in the tunnel roof in Stripsa research mine in Sweden. If we use the maximum discharge measured per unit width of a fracture (\( \sim 2.2 \times 10^{-7} \) m\(^3\)s\(^{-1}\)m\(^{-1}\)) and a hydraulic gradient of unity at the tunnel roof, the maximum fracture aperture is found to be \( \sim 295 \) \( \mu \)m. Moreno et al. (1990) found that the apertures vary between 200 and 300 \( \mu \)m in the Stripsa tunnel drift, whereas Abelin et al. (1985) gave a value as low as 10 \( \mu \)m.

Another factor is that the hydraulic gradient in the parent bedrock is much lower than along a tunnel mantle area. Neretnieks (1987) suggests that a plausible value of the hydraulic gradient in the bedrock at the depth of the repository would be \( \sim 0.4\% \). If this value is used in combination with the Pouiseuille flow equation, one obtains \( u = 34 \) h\(^2\). This relationship is definitely limited by the conditions discussed here, but is used in the sensitivity analysis to provide a basis for an 'order of magnitude analysis'.

As can be seen from the values in Table 7, the impact of the heterogeneity of the rock properties on the residence time PDF diminishes with increasing fracture aperture. Significant effects are obtained, however, for fracture apertures smaller than a few tenths of a millimetre for the conditions prevailing in the Swedish granitic bedrock. Particularly large deviations arise in the skewness between the homogeneous and the heterogeneous cases. The variances and the correlation lengths of \( \tilde{u}, \tilde{h} \) and \( \tilde{M} \), respectively, have the same effect on the residence time PDF, as is clear from (41) and (42). However, based on the specific statistic used here, the four terms of \( H_i \) that reflect heterogeneity of the rock property \( \tilde{M} \) contribute to about 25\% of the total sum.
Table 7 Effect analyses of the heterogeneous matrix diffusion for different fracture aperture and sorption characteristics. The following parameter values apply: $\varepsilon/\varepsilon_t = 1$, $D_p = 10^{-10}$ m$^2$/s, $L = 0.02$m, $\varepsilon_t = 0.005$, $\sum(\ell_i b_i) = 0.21$ and $\sum(\ell_i^2 b_i) = 0.032$. Further, a rapid sorption is assumed; $k_r \rightarrow \infty$.

<table>
<thead>
<tr>
<th>$h$ [m]</th>
<th>$u$ [m/s]</th>
<th>$u$ [m/year]</th>
<th>$\frac{2\varepsilon D_p}{huL}</th>
<th>\frac{\sigma_i^2}{\sigma^2_{(\ell=0)}}</th>
<th>S_i</th>
<th>S_i(\ell_i = b_i = 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00E-05</td>
<td>3.40E-09</td>
<td>1.07E-01</td>
<td>2.94E+03</td>
<td>1.85E+03</td>
<td>2.08E+06</td>
<td></td>
</tr>
<tr>
<td>3.00E-05</td>
<td>3.06E-08</td>
<td>9.65E-01</td>
<td>1.09E+02</td>
<td>6.96E+01</td>
<td>2.96E+03</td>
<td></td>
</tr>
<tr>
<td>9.00E-05</td>
<td>2.75E-07</td>
<td>8.69E+00</td>
<td>4.03E+00</td>
<td>3.54E+00</td>
<td>9.14E+00</td>
<td></td>
</tr>
<tr>
<td>2.70E-04</td>
<td>2.48E-06</td>
<td>7.82E+01</td>
<td>1.49E-01</td>
<td>1.09E+00</td>
<td>1.16E+00</td>
<td></td>
</tr>
<tr>
<td>8.10E-04</td>
<td>2.23E-05</td>
<td>7.03E+02</td>
<td>5.53E-03</td>
<td>1.00E+00</td>
<td>1.01E+00</td>
<td></td>
</tr>
<tr>
<td>2.43E-03</td>
<td>2.01E-04</td>
<td>6.33E+03</td>
<td>2.05E-04</td>
<td>1.00E+00</td>
<td>1.00E+00</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 17 Breakthrough curves in a 30-metre-long fracture for two identical cases with regard to the mean values of the parameters, but in which the rock properties are either heterogeneous or homogeneous. The same parameter values are used as for the 90 µm fracture accounted for in Table 5: $u = 8.7$ m/year, $\varepsilon/\varepsilon_t = 1, D_p = 10^{-10}$ m$^2$/s, $L = 0.02$ m, $\varepsilon_t = 0.005$, $k_r \rightarrow \infty$, $\sum(\ell_i b_i) = 0.21$ and $\sum(\ell_i^2 b_i) = 0.032$.

of $H_i$. Hence, heterogeneity of $\tilde{M}$ contributes to 25% of the total effect of the heterogeneous rock properties on the variance of the travel time PDF. Heterogeneity of $\tilde{u}$ and $\tilde{h}$ jointly contributes to the remaining 75%.

Fig. 17 shows the mean value solution $E[c(x,t)]$ obtained by the numerical inversion (Hollenbeck, 1998) of the heterogeneous case using the statistics and the parameter
values given in Table 7 for the 90 µm fracture. The homogeneous case exhibits a more pronounced peak concentration than the heterogeneous case, which is consistent with the difference of the temporal moments described above. The tail concentrations are particularly important for the estimation of the period of time during which a limiting concentration is exceeded.
6. Conclusions

An improved quantitative understanding of the effect of spatial heterogeneity of rock properties on the transport of radionuclides in fractures has been achieved through the execution of this project. The knowledge of the effect of uncertainty in heterogeneous rock properties on the transport of radionuclides in fractures is therefore essential for the performance assessment. The main contributions/analyses and results in this study are:

- This study presents the first analysis of the impact of heterogeneous mass transfer on the transport of radionuclides in rock fractures, in which most of the relevant rock properties such as aperture, porosity, effective diffusivity, sorption capacity and maximum diffusion depth are defined as spatially random. By using the Taylor expansion of the auxiliary variable $\beta$ in (9), the auto-covariance of $\beta$ could/can be approximated.

- An empirical database of the spatial variability of rock properties in a single fracture is obtained from various measurements on a large number of rock slabs taken at Åspö Hard Rock Laboratory, Sweden. The auto-covariance functions of rock properties can be used as a basis for the theoretical analyses of the effect of heterogeneous rock properties on radionuclide migration in fractured rock.

- Sorption kinetics of $^{137}$Cs on both intact and particle crystalline rock was measured in laboratory experiments. Surface sorption kinetics, which is predominantly governed by the rate-limited processes on the solid surface, was determined by means of bath tests with crushed rock particles. Particles were sufficiently small so that their external surface area is much larger than the internal surface area of the particle. The sorption kinetics relating to the intact rock reflects the combination of surface sorption and migration along intra-granular micro-fissures. The surface sorption rate for $^{137}$Cs on granite rock particles is 2 or 3 orders of magnitude higher than the sorption rate determined for intact rock. The adsorption rate applicable for Cs and intact Åspö diorite appears to lie in the range $4.6 \times 10^{-9} \text{ s}^{-1} < k_f < 2.8 \times 10^{-8} \text{ s}^{-1}$.

- The effect of the aspect ratio on the shear dispersion was studied by means of numerical experiments based on the mathematical formulation derived from the classic assumption of Taylor, but here in two dimensions. Numerical experiments were performed to estimate the shear dispersion caused by various aspect ratios of the cross-section in a rectangular conduit with laminar flow. The results show that a widely used form solution derived on the assumption of infinite width applies with an acceptable degree of accuracy only if the aspect ratio is less than about 10$^{-3}$. The maximum deviation between our prediction of the dispersion coefficient and the closed-form solution with infinite width can be a factor of 7, when the aspect ratio of the cross-section of a rectangular conduit is 0.06. This knowledge can be used to quantitatively estimate the dispersion coefficient in laboratory migration experiments.
Closed-form solutions are derived for the central temporal moments one to three of the residence time PDF for a pulse travelling in a rock fracture under the effect of heterogeneous mass transfer with the rock matrix. The solutions take into account effects of the actual (real) spatial parameter variability of properties along an individual transport path and effects due to the uncertainty in our knowledge of the heterogeneous rock properties. The mathematical formulation of the mass transfer problem includes one-dimensional advection along transport paths in a fracture, a diffusive flux directed laterally into the rock matrix and sorption kinetics in the rock matrix. The solutions are derived using exponential auto-covariance functions for all properties derived from data obtained from bedrock samples taken at Åspö Hard Rock Laboratory. The auto-covariances are represented individually for the advection velocity in the fracture, the fracture aperture and a typical matrix property including the effective diffusivity and the sorption partition coefficient. The definition of both the typical matrix property and the exponential covariance functions can most likely be generalised to several rock types.

Interpretations of Eqs. (42) and (43) suggest that the main effect of heterogeneity of the rock properties is due to the uncertainty in the properties associated with a discrete sampling technique; this is the effect accounted for by the H-terms in the solutions. If the rock properties are completely uncorrelated ($\ell_i=0$), uncertainty does not make any contribution to the effect of parameter variability on the solution. However, there is still an effect of the actual (real) spatial parameter variability along the transport paths.

Based on the data typical of Swedish crystalline bedrock, the error introduced in the variance of the residence time PDF by disregarding the effect of heterogeneity of the rock properties on the radionuclide migration is likely to be several hundred percent or more in fractures thinner than 100 µm. Upscaling of these small-scale transport phenomena investigated in this study into a PA model requires more advanced flow models than that employed in this study.
7. References


8. Appendix A  Definition of typical parameters

Table A-1 Definition of correlation length $\ell_i$ and typical parameters $a_i$ and $b_i$ in the auto-covariance of $\beta$ derived by using the Taylor expansion approach.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$a_i$</th>
<th>$b_i$</th>
<th>$\ell_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$d_i^2 + \left( E \left[ \eta_{M_1} \right] \right) l_2 + E \left[ \eta_{M_2} \right] l_3 + E \left[ \eta_{M_3} \right] l_4 \right) b_i$</td>
<td>$\text{Var}[u/\tilde{u}]$</td>
<td>$\ell_u$</td>
</tr>
<tr>
<td>2</td>
<td>$(E \left[ \eta_{M_1} \right] l_2 + E \left[ \eta_{M_2} \right] l_3 + E \left[ \eta_{M_3} \right] l_4 \right) b_i$</td>
<td>$E^2[\eta_i E^2 \eta / h \tilde{h}] \text{Var}[h / \tilde{h}]$</td>
<td>$\ell_h$</td>
</tr>
<tr>
<td>3</td>
<td>$(E \left[ \eta_{M_1} \right] l_2 + E \left[ \eta_{M_2} \right] l_3 + E \left[ \eta_{M_3} \right] l_4 \right) b_i$</td>
<td>$\text{Var}[u/\tilde{u}] \text{Var}[h / \tilde{h}]$</td>
<td>$\frac{1}{1 / \ell_u + 1 / \ell_h}$</td>
</tr>
<tr>
<td>4</td>
<td>$(d_i)^2 b_4$</td>
<td>$E^2 \left[ \tilde{M} / M \right] E^2 \left[ \eta_{ab} \right]$</td>
<td>$\ell_{L_1}$</td>
</tr>
<tr>
<td>5</td>
<td>$(d_i)^2 b_5$</td>
<td>$\text{Var}[\tilde{L}_1 / L_1]$</td>
<td>$\ell_{M_1}$</td>
</tr>
<tr>
<td>6</td>
<td>$(d_i)^2 b_6$</td>
<td>$E^2[\eta_{ab}] \text{Var}[\tilde{M}_1 / M_1]$</td>
<td>$\frac{1}{1 / \ell_{M_1} + 1 / \ell_{L_1}}$</td>
</tr>
<tr>
<td>7</td>
<td>$(d_i)^2 b_7$</td>
<td>$E^2[u/\tilde{u}] \text{Var}[h / \tilde{h}]$</td>
<td>$\frac{1}{1 / \ell_{M_1} + 1 / \ell_h}$</td>
</tr>
<tr>
<td>8</td>
<td>$(d_i)^2 b_8$</td>
<td>$\text{Var}[h / \tilde{h}] \text{Var}[\tilde{L}_1 / L_1]$</td>
<td>$\frac{1}{1 / \ell_h + 1 / \ell_{L_1}}$</td>
</tr>
<tr>
<td>9</td>
<td>$(d_i)^2 b_9$</td>
<td>$E^2[u/\tilde{u}] \text{Var}[h / \tilde{h}]$</td>
<td>$\frac{1}{1 / \ell_{L_1} + 1 / \ell_h + 1 / \ell_{M_1}}$</td>
</tr>
<tr>
<td>10</td>
<td>$(d_i)^2 b_{10}$</td>
<td>$E^2[h / \tilde{h}] \text{Var}[u / \tilde{u}]$</td>
<td>$\frac{1}{1 / \ell_{M_1} + 1 / \ell_u}$</td>
</tr>
<tr>
<td>11</td>
<td>$(d_i)^2 b_{12}$</td>
<td>$E^2 \left[ \tilde{M} / M \right] E^2 \left[ u / \tilde{u} \right]$</td>
<td>$\frac{1}{1 / \ell_{L_1} + 1 / \ell_u}$</td>
</tr>
<tr>
<td>12</td>
<td>$(d_i)^2 b_{12}$</td>
<td>$\text{Var}[h / \tilde{h}] \text{Var}[u / \tilde{u}]$</td>
<td>$\frac{1}{1 / \ell_u + 1 / \ell_{L_1} + 1 / \ell_{M_1}}$</td>
</tr>
<tr>
<td>13</td>
<td>$(d_i)^2 b_{13}$</td>
<td>$\text{Var}[u / \tilde{u}] \text{Var}[h / \tilde{h}]$</td>
<td>$\frac{1}{1 / \ell_u + 1 / \ell_h + 1 / \ell_{M_1}}$</td>
</tr>
<tr>
<td>14</td>
<td>$(d_i)^2 b_{14}$</td>
<td>$E^2 \left[ \tilde{M} / M \right] \text{Var}[u / \tilde{u}]$</td>
<td>$\frac{1}{1 / \ell_u + 1 / \ell_h + 1 / \ell_{L_1}}$</td>
</tr>
<tr>
<td>15</td>
<td>$(d_i)^2 b_{15}$</td>
<td>$\text{Var}[u / \tilde{u}] \text{Var}[h / \tilde{h}]$</td>
<td>$\frac{1}{1 / \ell_u + 1 / \ell_h + 1 / \ell_{M_1} + 1 / \ell_{L_1}}$</td>
</tr>
</tbody>
</table>
Table A-2 Definition of correlation length $\ell_i$ and typical parameters $a_i$ and $b_i$ in Eq. (46).

<table>
<thead>
<tr>
<th>i</th>
<th>$a_i$</th>
<th>$b_i$</th>
<th>$\ell_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$(d_1 + E[\eta_{M,h}]d_2 + E[\eta_{M,h}]d_3 + E[\eta_{M,h}]d_4)b_1$</td>
<td>$\text{Var}[u/\tilde{u}]$</td>
<td>$\ell_u$</td>
</tr>
<tr>
<td>2</td>
<td>$(d_2^2 + d_3^2 + d_4^2)b_2$</td>
<td>$E^2[\tilde{M}/M]E^2[\eta_h]\text{Var}[\tilde{h}/\tilde{h}]$</td>
<td>$\ell_h$</td>
</tr>
<tr>
<td>3</td>
<td>$(d_2^2 + d_3^2 + d_4^2)b_3$</td>
<td>$E^2[\tilde{M}/M]\text{Var}[u/\tilde{u}]\text{Var}[\tilde{h}/\tilde{h}]$</td>
<td>$\frac{1}{1/\ell_u + 1/\ell_h}$</td>
</tr>
<tr>
<td>4</td>
<td>$(d_2^2)b_4$</td>
<td>$E^2[\eta_h]E^2[\tilde{h}/\tilde{h}]\text{Var}[\tilde{M}_i/M_i]$</td>
<td>$\ell_{M_1}$</td>
</tr>
<tr>
<td>5</td>
<td>$(d_2^2)b_5$</td>
<td>$E^2[\eta_h]\text{Var}[\tilde{h}/\tilde{h}]\text{Var}[\tilde{M}_i/M_i]$</td>
<td>$\frac{1}{1/\ell_{M_1} + 1/\ell_h}$</td>
</tr>
<tr>
<td>6</td>
<td>$(d_2^2)b_6$</td>
<td>$E^2[\eta_h]\text{Var}[u/\tilde{u}]\text{Var}[\tilde{M}_i/M_i]$</td>
<td>$\frac{1}{1/\ell_u + 1/\ell_h}$</td>
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<tr>
<td>7</td>
<td>$(d_2^2)b_7$</td>
<td>$\text{Var}[u/\tilde{u}]\text{Var}[\tilde{h}/\tilde{h}]\text{Var}[\tilde{M}_i/M_i]$</td>
<td>$\ell_{M_2}$</td>
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<td>$\frac{1}{1/\ell_{M_2} + 1/\ell_h}$</td>
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<td>9</td>
<td>$(d_2^2)b_9$</td>
<td>$E^2[\eta_h]E^2[\tilde{h}/\tilde{h}]\text{Var}[\tilde{M}_2/M_2]$</td>
<td>$\frac{1}{1/\ell_u + 1/\ell_h}$</td>
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<td>10</td>
<td>$(d_2^2)b_{10}$</td>
<td>$E^2[\eta_h]\text{Var}[u/\tilde{u}]\text{Var}[\tilde{M}_2/M_2]$</td>
<td>$\ell_{M_3}$</td>
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<tr>
<td>11</td>
<td>$(d_2^2)b_{11}$</td>
<td>$\text{Var}[u/\tilde{u}]\text{Var}[\tilde{h}/\tilde{h}]\text{Var}[\tilde{M}_2/M_2]$</td>
<td>$\frac{1}{1/\ell_u + 1/\ell_h + 1/\ell_{M_3}}$</td>
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<td>12</td>
<td>$(d_2^2)b_{12}$</td>
<td>$E^2[\eta_h]E^2[\tilde{h}/\tilde{h}]\text{Var}[\tilde{M}_3/M_3]$</td>
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<td>$E^2[\eta_h]\text{Var}[\tilde{h}/\tilde{h}]\text{Var}[\tilde{M}_3/M_3]$</td>
<td>$\frac{1}{1/\ell_{M_3} + 1/\ell_h}$</td>
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<td>14</td>
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<td>$(d_2^2)b_{15}$</td>
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<td>$\frac{1}{1/\ell_u + 1/\ell_h + 1/\ell_{M_3}}$</td>
</tr>
</tbody>
</table>
9. Appendix B  Notation

a  constant in Eq. (58)

a_i auxiliary variable in Eq. (10)

A_E total external geometric surface area, [m^2], in Eq. (58)

A_{ES} geometric surface of a sphere with the same size as that of the mean particle, [m^2], in Eq. (58)

A_{IN} internal surface area, [m^2]

A_T physical surface area, [m^2], in Eq. (58)

b_i auxiliary variable in Table 1

c concentration in main fracture defined as mass/activity per unit volume of water, [kg/ m^3]

c_a concentration defined as adsorbed solute mass per unit bulk volume of medium, [kg/ m^3]

c_d concentration defined as dissolved solute mass per unit volume of medium, [kg/ m^3]

c_e concentration of mobile phase of solute, [kg/ m^3]

c_m concentration defined as dissolved solute mass per unit volume of water, [kg/ m^3]

c_s concentration defined as adsorbed mobile solute mass per unit solid mass, [kg/kg]

c_w concentration defined as adsorbed (fixed) solute mass per unit solid mass, [kg/kg]

C1, C2 constants in Eq. (22)

D molecular (ionic) diffusivity, [m^2/s]

D_e effective diffusivity, [m^2/s], D_e = ε_t D_p

D'_e effective diffusivity taking into account surface diffusion, D'_e = ε_t D_p + k_d1 ρ D_s, [m^2/s]

D_p pore diffusivity, D_p =D\delta_D/\tau^2, [m^2/s]

D_s surface diffusivity, [m^2/s]

D_{s0} arithmetic mean of the particle diameter

E dispersion coefficient, [m^2/s]

f(t) probability density function for residence time

g(τ) travel time PDF of inert particles

h fracture aperture, [m]

H heigh of vertical aperture [m]

H_i typical parameters reflecting uncertainty of heterogeneous rock properties

i,k indices

k_d partition coefficient, k_d = c_w/c_m, [m^3/kg]

k_{d1} partition coefficient, k_{d1} = c_s/c_m, [m^3/kg]

K_D partition coefficient, K_D = ρ/ε_k_a, [-]

k_r adsorption rate coefficient, [s^{-1}]

L extension of rock matrix, [m]

M_0 total injected solute mass, [kg]

M effective matrix property in Eq. (22)

M_1,M_2,M_3 effective matrix property in Eq. (34)
nk $^{k}$th temporal moment in Eq. (35)
l thickness of the slab, [m], in Eq. (56)
p Laplace transform variable
p pressure, [Pa], in Eq. (49)
$P_E$ peak value of concentration distribution with equilibrium chemistry
$P_k$ peak value of concentration distribution with kinetics
Q water flow, [m$^3$/s], in Eq. (4)
$Q_T$ total amount of diffusing substance, [kg/ m$^2$], in Eq. (56)
R retardation factor [-]
$S_t$ skewness, [s$^3$], in Eq. (38)
t time [s]
T typical residence time for solute transport in the rock matrix [s]
u advective velocity, [m/s]
W width [m]
x, y Cartesian co-ordinate, [m]
z co-ordinate, [m] perpendicular to the main direction of the flow

$\alpha$ auxiliary variable in Eq. (10)
$\beta$ auxiliary variable in Eq. (9)
$\delta$ Dirac delta function
$\delta_D$ constrictivity
$\varepsilon$ porosity of rock
$\varepsilon_{\text{peak}}$ relative error in the peak value resulting from the assumption of equilibrium chemistry
$\varepsilon_{\text{var}}$ relative error in the variance resulting from the assumption of equilibrium chemistry
$\varepsilon_t$ porosity available for transport
$\zeta_1$ auxiliary variable in Eq. (55)
$\zeta_2$ auxiliary variable in Eq. (55)
$\eta$ auxiliary variable in Eq. (22)
$\kappa$ sorption capacity factor, [-], in Eq. (56)
$\lambda$ rate of radioactive decay, [s$^{-1}$]
$\lambda_g$ surface roughness factor in Eq. (58)
$\mu$ dynamic viscosity, [Pa s]
$\mu_t$ expected residence time, [s]
$\xi$ trajectory co-ordinate, [m]
$\rho$ density of the rock, [kg/ m$^3$]
$\sigma_r^2$ variance of residence time, [s$^2$]
$\sigma_{r,\varepsilon}^2$ variance of residence time resulting from the assumption of equilibrium chemistry, [s$^2$]
$\sigma_{r,k}^2$ variance of residence time resulting from the assumption of kinetic adsorption, [s$^2$]
$\tau$ tortuosity
$\tau$ travel time, [s], in Eq. (50)
Ψ auxiliary variable in Eq. (3a)
Ψ₁, Ψ₂ typical parameters reflecting the kinetics of the sorption process
Ω auxiliary variable in Eq. (3a)