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Validation of matrix diffusion modeling

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ABSTRACT

Crystalline rock has been chosen as the host medium for repository of highly radioactive spent nuclear fuel in Finland. Radionuclide transport takes place along water-carrying fractures, and matrix diffusion has been indicated as an important retarding mechanism that affects the transport of mobile fission and activation products. The model introduced here for matrix diffusion contains a flow channel facing a porous matrix with stagnant water into which tracer molecules advected in the channel can diffuse. In addition, the possibility of a finite depth of the matrix and an initial tracer distribution ('contamination') in the matrix are included in the model.

In order to validate the developed matrix diffusion model, a relatively simple measuring system was constructed. Matrix diffusion was illustrated by observing the migration of 0.1 ml KCl pulses in the water flowing through a channel facing a porous matrix made of synthetic fibre felt. Migration of K^+ and Cl^- ions was monitored by measuring the electrical conductivity of the solution. The experimental system allowed also measurements on the concentration profile inside the porous matrix, but the focus is here on the input and output (breakthrough) pulses. Measurements were performed for two different initial distributions of KCl tracer in the porous matrix. There was excellent agreement between modeling and experimental results with consistent values for the diffusion coefficient used as the fitting parameter.

1. Introduction

Matrix diffusion has received notable research interest over the past three decades (e.g. Foster, 1975; Norton and Knapp, 1977; Neretnieks, 1980; Wood et al., 1990; Guimera and Carrera, 2000). This research has mainly focused on matrix diffusion in crystalline and sedimentary rocks since many countries have decided or are planning to build nuclear waste repositories in these kinds of formation (e.g. Skagius and Neretnieks, 1986; Guimera and Carrera, 2000; Shapiro, 2001; Neretnieks, 2002). As man-made constructions may eventually break, radioactive pollutants may get in contact with groundwater. This would cause migration of nuclear waste through soil, which may pose a threat to water resources and nature. Therefore, estimation of the sphere of influence of nuclear waste is essential. Retardation processes caused by matrix diffusion and sorption are believed to be significant in the migration of radionuclides in the geosphere.

The time perspective of the safety assessments of nuclear waste repositories spans up to 250 000 years including at least one glaciation. At the moment there is an ongoing research and discussion in Finland and Sweden on the influence of ice age on the safety of nuclear waste repositories. In this work we have thus measured and modeled a situation where fresh water is introduced to an initially contaminated matrix. This might be the case when an upcoming ice age is drawing back and fresh melting water is getting in touch with the repository system. Also, in many in situ (Hodgkinson et al., 2009) and laboratory-scale (Hölttä et al., 1992; Siitari-Kauppi et al., 1997) experiments it would be advantegeous to use tracers which already exist in the environment or the sample, especially when repeated influxes of tracers are used.

Usually matrix diffusion problems have been solved by numerical methods (e.g. Chittaranjan et al., 1997; Hadermann and Heer, 1996; Kennedy and Lennox, 1995; Doughty, 1999), by random walk methods (e.g. Painter et al., 2008; Delay et al., 2008) or by Laplace transforms (e.g. Tang et al., 1981; Cvetkovic et al., 1999). These methods have typically been used in specific experimental set-ups or for making modeling predictions. So far there have been analytical solutions available for advection–diffusion systems only in the simple situation of an infinite immobile zone (Neretnieks, 1980). Analytical or semi-analytical solutions for more generic situations which more often appear in real life are therefore called for, as they can be more effectively applied in safety analysis or

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performance assessment. Furthermore, a common framework allowing an efficient numerical implementation, which would also allow for inclusion of many different phenomena that may occur, would be advantageous.

To this end we consider in this work matrix diffusion of a non-radioactive and inert tracer in the situation where the porous matrix already contains a distribution of the tracer before a sharp pulse of it is injected into the flow. We thus expect to see a breakthrough curve which is a sum of two components. This problem is a continuation to an earlier work of ours in which a generic framework for matrix diffusion problems is discussed, but there a 'clean' matrix before introduction of a tracer pulse was only considered (Kekäläinen et al., submitted for publication). Complexity of the system is now increased so as to test the limits of the model developed.

We provide a new semi-analytic solution to the advection–diffusion equations in the case of a well mixed flow past a porous matrix. Solution is based on a Laplace transform of the equation and on using appropriate dimensionless variables. The main advantage of the model is that arbitrary boundary and initial conditions can be used so that it can better be used to model, e.g. in situ bedrock experiments. It is evident that such experiments require well-designed set-ups and carefully selected parameters in order to enable detection of effects caused by matrix diffusion.

We also perform laboratory-scale experiments to validate the modeling. A specific measuring system is constructed in which the tracer concentration can be monitored in the flow channel and in the porous matrix. This allows experiments in which the initial concentration of the tracer in the matrix can be reliably controlled.

2. Mathematical model

The solution to a similar problem with a vanishing initial concentration of tracer in the porous matrix has been given in (Kekäläinen et al., submitted for publication). Here we derive the solution for a general initial concentration distribution, $C_0(x,z)$, in the matrix.

2.1. Matrix of finite depth

Consider the case in which the matrix of porous medium around a flow channel has a finite depth, L_z, in the z direction. If we only consider advection of the tracer in the flow channel in the x direction, and its transverse diffusion in the matrix, its concentration in the flow channel, C, and in the porous matrix, C_m, are governed by the equations (Neretnieks, 1980)

$$\begin{aligned}
&\frac{\partial C}{\partial t}(x,t) + v\frac{\partial C}{\partial x}(x,t) = \frac{\epsilon D}{b}\frac{\partial C_m}{\partial z}(x,0,t) \\
&\frac{\partial C_m}{\partial t}(x,z,t) - D\frac{\partial^2 C_m}{\partial z^2}(x,z,t) = 0
\end{aligned} \tag{2.1}$$

with the boundary and initial conditions, in the general case when there is also an initial tracer distribution in the porous matrix,

$$\begin{aligned}
&C_m(x,z,0) = C_0(x,z) \quad C(x,0) = C_0(x,0) \\
&C_m(x,0,t) = C(x,t) \quad C(0,t) = C_1(t) \\
&\frac{\partial C_m}{\partial z}(x,L_z,t) = 0
\end{aligned} \tag{2.2}$$

Here D is the diffusion constant of the tracer in the matrix, v the flow velocity in the channel, C_0 the initial tracer concentration in the matrix, and C_1 the input concentration of tracer into the channel. We are here interested in C at the end of the flow channel, $C(L,t)$, i.e. the breakthrough curve.

The diffusion equation for $C_m(x,z,t)$ can be solved by separation of variables, and the solution is a sum of two contributions,

$$C_m = C_m^{(1)} + C_m^{(2)} \tag{2.3}$$

such that

$$\begin{aligned}
&C_m^{(1)}(x,z,0) = C(x,0) \quad C_m^{(2)}(x,z,0) = C_0(x,z) - C_0(x,0) \\
&C_m^{(1)}(x,0,t) = C(x,t) \quad C_m^{(2)}(x,0,t) = 0 \\
&\frac{\partial C_m^{(1)}}{\partial z}(x,L_z,t) = 0 \quad \frac{\partial C_m^{(2)}}{\partial z}(x,L_z,t) = 0
\end{aligned} \tag{2.4}$$

The solution to these boundary value problems is given by

$$C_m^{(1)}(x,z,t) = C(x,t) - \frac{2}{L_z}\int_0^t \left(\sum_{n=0}^{\infty} \frac{1}{\lambda_n} e^{-D\lambda_n^2(t-s)} \sin\lambda_n z\right)\frac{\partial C}{\partial s}(x,s)ds \tag{2.5}$$

and

$$C_m^{(2)}(x,z,t) = \frac{2}{L_z}\sum_{n=0}^{\infty}\left(\int_0^{L_z}(C_0(x,y) - C_0(x,0))\sin\lambda_n y\, dy\right)e^{-D\lambda_n^2 t}\sin\lambda_n z \tag{2.6}$$

where

$$\lambda_n = \frac{(2n+1)\pi}{2L_z} \tag{2.7}$$

Substituting $C_m(x,z,t)$ into Eq. (2.1), we find a closed expression for C,

$$\begin{aligned}
\frac{\partial C}{\partial t}(x,t) + v\frac{\partial C}{\partial x}(x,t) = &-\frac{2\epsilon D}{L_z b}\int_0^t\left(\sum_{n=0}^{\infty} e^{-D\lambda_n^2(t-s)}\right)\frac{\partial C}{\partial s}(x,s)ds \\
&+ \frac{2\epsilon D}{L_z b}\int_0^{L_z}(C_0(x,y) \\
&- C_0(x,0))\left(\sum_{n=0}^{\infty}\lambda_n e^{-D\lambda_n^2 t}\sin\lambda_n y\right)dy
\end{aligned} \tag{2.8}$$

Introducing dimensionless variables,

$$\xi = \frac{x}{L}, \quad \tau = \frac{tv}{L}, \quad \zeta = \frac{y}{L_z} \tag{2.9}$$

Eq. (2.8) can be expressed in the form

$$\begin{aligned}
\frac{\partial C}{\partial \tau}(\xi,\tau) + \frac{\partial C}{\partial \xi}(\xi,\tau) = &-\frac{2\lambda}{\kappa}\int_0^{\tau}\left(\sum_{n=0}^{\infty} e^{-(\gamma_n^2/\kappa^2)(\tau-\sigma)}\right)\frac{\partial C}{\partial \sigma}(\xi,\sigma)d\sigma \\
&+ \frac{2\lambda}{\kappa}\int_0^1 (F(\xi,\zeta) - F(\xi,0)) \\
&\times\left(\sum_{n=0}^{\infty}\gamma_n e^{-(\gamma_n/\kappa)^2\tau}\sin\gamma_n\zeta\right)d\zeta
\end{aligned} \tag{2.10}$$

with the initial and boundary conditions

$$C(\xi,0) = F(\xi,0), \quad C(0,\tau) = f(\tau) \tag{2.11}$$

Here we have used the dimensionless parameters

$$\lambda = \epsilon\frac{L}{b}\sqrt{\frac{D}{Lv}}, \quad \kappa = \frac{L_z}{L}\sqrt{\frac{Lv}{D}}, \quad \gamma_n = \left(n + \frac{1}{2}\right)\pi \tag{2.12}$$

and

$$F(\xi,\zeta) = C_0(x,y), \quad f(\tau) = C_1(t) \tag{2.13}$$

Laplace transformation of Eq. (2.10) with respect to variable τ gives

$$\begin{aligned}
&\frac{\partial \widehat{C}}{\partial \xi}(\xi,s) + \left(s + \lambda\sqrt{s}\tanh\left(\kappa\sqrt{s}\right)\right)\widehat{C}(\xi,s) = G(\xi,s) \\
&\widehat{C}(0,s) = \hat{f}(s)
\end{aligned} \tag{2.14}$$