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# Determination of sorption properties of intact rock samples: New methods based on electromigration

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Two new methods for determining sorption coefficients in large rock samples have been developed. The methods use electromigration as a means to speed up the transport process, allowing for fast equilibration between rock sample and tracer solution. An electrical potential gradient acts as a driving force for transport in addition to the concentration gradient and forces the cations through the rock sample towards the cathode. The electrical potential gradient induces both electromigration and electroosmotic flow with a resulting solute transport that is large compared to diffusive fluxes. In one of the methods, the solute is driven through the sample and collected at the outlet side. In the other, simpler method, the rock sample is equilibrated by circulating the solute through the sample. The equilibration of rock samples, up to 5 cm in length, with an aqueous solution has been accomplished within days to months. Experiments using cesium as a sorbing tracer yield results consistent with considerably more time demanding in-diffusion experiments. These methods give lower distribution coefficients than those obtained using traditional batch experiments with crushed rock.

## 1. Introduction

Sorption is one of the most important processes retarding radionuclide transport in fractured crystalline rock. Practically all available sorption data have been obtained from laboratory experiments using crushed rock (Bradbury and Baeyens, 1997; Carbol and Engkvist, 1997; Crawford et al., 2006). However, the sample preparation of such traditional sorption experiments could change the sorption properties of the rock sample. Thus, methods are needed by which the sorption properties of intact rock samples can be determined.

One of the main concerns with traditional batch sorption experiments is the crushing of the rock sample to fine particles. The crushing process creates new surfaces that significantly increases the specific surface area of the sample and may give access to otherwise isolated pores. The new surfaces created may also have different sorption properties than the indigenous rock surfaces. Most distribution coefficient reported in the literature are mass based and do not take into account the increase of specific surface area induced by the crushing process. This may lead to non-conservative sorption data (Johansson et al., 1998). For example, increase in specific surface area, with decreasing particle size, has been shown to increase mass-normalized sorption of cesium [$Cs^+$] and strontium (Skagius, 1986; Byegård et al., 1998).

In sorption experiments, the crushing of the rock sample is employed to reduce the diffusion length. By this, the experimental time is greatly reduced as the apparent diffusivity of sorbing cations in the rock matrix is low. Sorption experiments using intact rock samples have been recognized as advantageous as the artifacts related to the generation of new surfaces is minimized (Skagius et al., 1982). However, sorption experiments using intact rock samples demand long experimental times even for small samples because the diffusive transport of the tracer ions to the internal surfaces is slow. The drilling to extract the drillcore and the sawing performed to obtain shorter samples has been shown to alter some of the properties of the rock. The disturbed zone can extend millimetres up to centimetres into

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the rock from sawed or drilled surfaces (Autio et al., 1998). This indicates that it is of interest to perform experiments with intact rock samples in the centimetre range.

Faced with this problem, Löfgren and Neretnieks (2004), proposed the use of electromigration as a way of reducing the experimental time whilst still being able to perform experiments with large intact rock samples. In this method, the flux of the charged species is increased by applying an electric field over the intact rock sample. The method of using electromigration to increase the rate of migration has previously been used to determine diffusional properties in Boom Clay using sorbing species, such as strontium (Maes et al., 1999). Here, we have modified the method to be applicable to low-porosity, crystalline rocks.

We have developed electromigration methods to allow determination of CEC as well as sorption distribution coefficients. Determinations of CEC for rock samples is of interest as it is possible that the CEC can be used to predict the sorption of ions in trace concentrations known to sorb primarily by cation exchange reactions.

This communication describes how electromigration can be used for rapid determinations of diffusional properties, sorption distribution coefficients, and cation exchange capacities of crystalline rock. Experimental results obtained using the electromigration methods are compared with results from traditional diffusion based methods in order to evaluate the performance of the developed method. Sorption results, both distribution coefficients and cation exchange capacities, determined using intact rock samples and $Cs^+$ as a sorbing tracer are compared to sorption results obtained from crushed rock samples of nearby locations of the same drillcores. This comparison is performed to evaluate if the crushing process affects the sorption properties of a low-porosity crystalline rock. The rock samples used in the experiments are taken from Äspö and Laxemar, two sites investigated for potential storage of nuclear waste in Sweden.

## 2. Theory: Transport of ions in an electric field and sorption

Most of the radionuclides of interest for the performance assessment of geological repositories for nuclear waste storage are positively charged and are sorbed onto the rock by cation exchange and/or by surface complexation. In this paper, we will focus on transport and sorption of charged species that mainly sorb by ion exchange.

Charged species are forced towards the electrode of opposite charge when subjected to an electric field. The migration velocities of the charged species depend on the electric field strength and the ionic mobility, $\mu$, of the species

$$\upsilon = -\mu \frac{d\phi}{dx} \tag{1}$$

where $\upsilon$ is the velocity and $\frac{d\phi}{dx}$ is the electric potential gradient. The flux of ions in a rock sample exposed to an electric field is given by,

$$j = -\mu_r c \frac{d\phi}{dx} \tag{2}$$

where $c$ is the concentration in the sample and $\mu_r$ is the mobility of the ions in the porous rock matrix. The flux can be converted into electric current using the geometry of the sample and Faraday's constant as follows,

$$I = A \cdot F \cdot j = -A \cdot F \cdot \mu_r c \frac{d\phi}{dx} \tag{3}$$

where $I$ is the current, $F$ is Faradays constant, and $A$ is the cross sectional area of the sample. The ionic mobility can be converted to a Fick's diffusion coefficient using the Einstein relation (Atkins, 1984),

$$D = \frac{\mu kT}{ze} \tag{4}$$

where $k$ is the Boltzmann constant, $T$ is the temperature, $z$ is the charge of the species, and $e$ is the electron charge. In addition to the ion transport in the pore solution, the usually negatively charged pore walls of the minerals give rise to an electrical double layer (EDL) which partly consists of mobile ions (Revil, 1999). When the mobile cations in the EDL are exposed to an electrical potential gradient they migrate towards the cathode, and due to viscous effects, induce a bulk flow of the pore solution. This electroosmotic flow (Eq. (5)) further increases the rate of migration of solutes in crystalline rock. The electroosmotic velocity, $\upsilon_{eo}$, varies with the potential gradient in the same way as the ionic velocity (Maes et al., 1999),

$$\upsilon_{eo} = -\mu_{eo} \frac{d\phi}{dx} \tag{5}$$

where $\mu_{eo}$ is the electroosmotic mobility. A mass balance accounting for transport and accumulation can be used to account for both diffusive mass transport and electromigration

$$\frac{\partial c}{\partial t}(\varepsilon + \rho K_d) = D_e \frac{\partial^2 c}{\partial x^2} + \frac{\partial}{\partial x}\left[c(\mu + \mu_{eo})\frac{d\phi}{dx}\right] \tag{6}$$

$$D_e = \varepsilon_t \cdot \frac{\delta_D}{\tau^2} \cdot D_w = F_f \cdot D_w \tag{7}$$

where $\varepsilon$ is the total porosity, $\varepsilon_t$ is the porosity associated with the transport through the rock sample, $D_w$ is the diffusion coefficient in water, $D_e$ is the effective diffusion coefficient, $\delta_D$ is the constrictivity, $\tau^2$ is the tortuosity, $F_f$ is the formation factor, and $\rho$ is the density of the rock sample.

The sorption properties of the rock can be described by the distribution coefficient, $K_d$,

$$K_d = \frac{c_s}{c_w} \tag{8}$$

where $c_s$ is the concentration in the solid phase and $c_w$ is the concentration in the bulk, aqueous solution. The distribution coefficient, $K_d$, is often concentration independent at low aqueous concentrations and in systems where the concentration of the tracer ion is small compared to the total ion concentration.

The cation exchange capacity (CEC) of a rock sample can be seen as a measure of the total amount of electrostatically sorbed ions (Stumm and Morgan, 1996). The amount of electrostatically sorbed ions is proportional to the sum of fixed surface