

## **Diffusive transport in low permeability transport**

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### **ABSTRACT**

Experiment effort to evaluate the barrier performance of geologic disposal requires relatively long testing periods and chemically stable conditions. We have applied a new technique, the micro-channel method to present a fast and sensitive method to measure both diffusivity and sorption coefficient within a week to overcome the disadvantage of the conventional method. In this method, a Teflon plate with a micro channel is placed beneath the rock sample plate, the solution with strontium is injected into the channel with constant rate. The breakthrough curve is obtained until steady state and the outlet flux does not meet the inlet flux simple due to the element loss from the channel into the rock sample. Then the fitting procedure is employed to speculate the Kd and De values.

### **INTRODUCTION**

#### **General Background**

Radioactive materials are used all over the world as fuel for nuclear reactors, in industrial processes, in research laboratories as well as in medical applications. All of these uses produce radionuclide waste in different forms; unlike ordinary laboratory debris these wastes cannot simply be discarded. Special treatment is required for any material that has been in contact with radioactive substances. Radioactive elements continuously decay at a specific characteristic rate. When waste is isolated for a long enough period (several half-lives) the radioactivity is severely attenuated, although the waste may retain its chemical toxicity indefinitely. The disposal problem is thus simplified for waste which only contain elements with short half-lives because the radioactive hazard only lasts a few years or decades. But for the radioactive elements which decay slowly, the radiation hazard of the waste extends to tens or hundreds of thousands of years. Therefore, guarantees must be given to isolate the waste from the human environment for an enormous length of time; this inherently makes the disposal of radioactive waste extremely difficult (Krauskopf, 1988). Is there enough geological and geochemical information to build confidence in such guarantees? Some argue that the uncertainties about geologic disposal are great enough to think about more radical radioactive waste treatment alternatives. For example, some suggestions include: 1) transmuted the elements

to reduce their radioactivity, or 2) sending the waste in rockets for extra-terrestrial disposal. However, the preferred option remains geologic disposal because of both the safety and economic issues pertinent to high-level radioactive waste management.

The site for high-level radioactive waste disposal should be isolated from the surface environment and this typically requires burial at depths of 500 m or more. The waste should be converted to a solid form before burial to ensure stability. Fluid access into the engineered barrier is one of the key risks. However, there is considerably less scientific information and engineering experience with disposal sites at depths below a few hundred meters. To examine whether the repository is sufficiently isolated, information is needed in several fields. The rate of dissolution of many radionuclides is strongly influenced by the flow rate and flow distribution at repository depth (Neretnieks, 1993). The travel time is affected by the flow path and velocity and longer residence times could allow more time for radionuclides to decay. Over time, axial dispersion and channeling have the same effect of diluting solute species, but may allow a fraction of the dissolved radionuclides to travel faster than average solvent velocity. Traverse dispersion also cause dilution but allows exchange between fast and slow paths. For the nuclides which sorb onto the fissure surface and diffuse into the rock matrix, the exposed geometric surface area and the microporous nature of these surfaces directly affects the contact area between

flowing water and rock. Specifically, a typical safety case should demonstrate that wastes are sequestered long enough for decay of the most active nuclides such as  $^{90}\text{Sr}$  and  $^{127}\text{Cs}$  and also ensure the dissolution and movement of radioactive material in ground water thereafter are sufficiently impeded.

**Specific background in the project**

A multi-barrier system comprising an engineered plus a natural barrier has been developed in the concept of deep underground geologic repositories for high level radioactive. To examine the safety of geologic disposal, the migration of leaked radionuclides from the repository and the transport with groundwater in fissures should be predictable. In fractured crystalline rocks, the radionuclides will be transported primarily by groundwater along fractures, but may also adsorb to the rock surface and absorb into micropores (Neretnieks, 1980). The interaction between the rock and the radionuclides serves to retard the migration of radionuclides compared to the velocity of the groundwater. This interaction has been estimated using the sorption coefficient (Kd) and the effective diffusion coefficient (De) which are the important factors in radionuclide retardation.

The engineered barrier and surrounding geological barrier may preclude the development of meso-scale fracture pathways, and therefore diffusive flux, although much slower than advection, must also be considered as an alternate risk for loss of containment, especially because of the extended period of time over which sequestration is required. Therefore over the last two decades, the important influence of matrix diffusion on transport has been shown in many theoretical and experimental studies (Bodin, Delay et al. 2003). During transport, diffusion mainly causes a slowdown in the migration of the solute and a decrease in concentration peaks, such effects are very important in assessing the risk of radionuclide leaks from the deep underground repository. Sudicky and Frind (1982) have shown that the travel times in the system with matrix diffusion are significantly larger than when only transport is taken into account in fractures. In crystalline rocks with lower matrix porosity, the role of diffusion remains significant. Novakowski and Bogan (1999) indicated that a matrix porosity of 1% may delay the concentration peaks by half an order of magnitude in time as well as lower the maximal concentrations by one order of magnitude for 100 m travel distance. Many factors related to the matrix porosity influence diffusion such as connected pore volume, tortuosity, and constrictivity. All the efforts to study the diffusion mechanism are complicated by the fact that diffusion is slow, concentrations expected in the fluid are low, and important heterogeneities exist within the solids of interest which makes

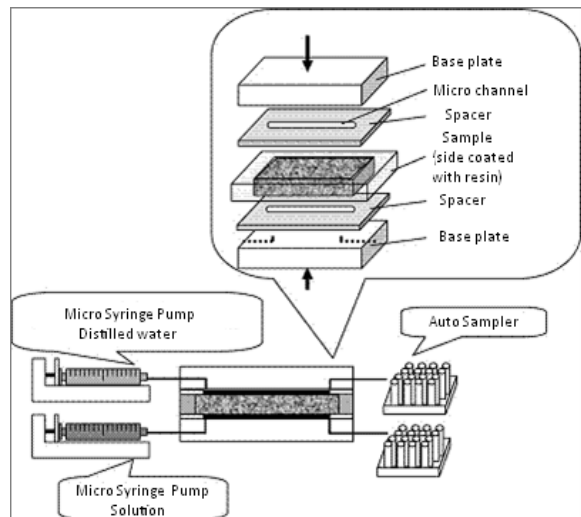
extrapolation from small physical reference volumes difficult.

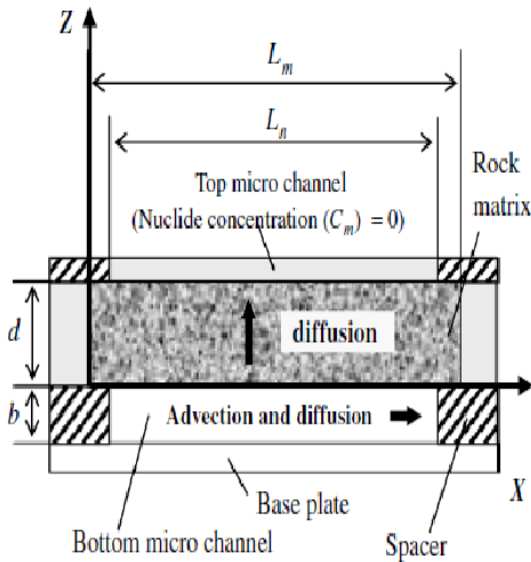
Therefore, a fast method has been developed referring to as the Micro-Reactor Simulated-Channel (MRSC) to determine both De and Kd simultaneously using non-crushed rock samples (Okuyama et al 2008). The concept of this method is similar to the micro chemical reactor, where a very thin fluid flow channel in the middle of the solid system increases the rate of surface reactions due to the high surface area to liquid volume ratio and this enables one to make fast measurements using only a small reactor volume. Installing the small reactor directly into an excavated deep borehole in the actual geologic environment provides the possibility for *in situ* measurement.

**METHOD AND MATERIAL**

**Micro-Reactor with Simulated Channel**

The new apparatus consists of two injection syringe pumps, a reaction unit, and two auto samplers as shown in Figure 1a. The reaction unit contains two base plates, two spacers with a micro channel at the center and rock sample coated with epoxy resin in the middle of the whole unit. The reason to have the coated epoxy at the side edge surfaces is to avoid the evaporation of the test solution during the experiment.





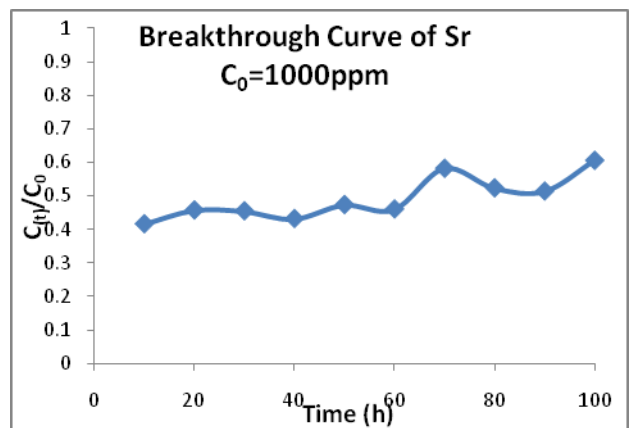
**Figure 1** a) the experiment set up for the micro-channel method; b) cross-sectional view of the experimental set up of rock sample and micro-flow channels (Okuyama et al 2008).

In this method, the spacer is made of a Teflon plate with a micro channel beneath the rock sample. A radionuclide-bearing solution is pumped into the channel at a constant rate. The breakthrough curve is monitored until steady state is reached. The outlet flux at steady state does not equal the inlet flux because of matrix diffusion from the micro channel into the surrounding rock body. If the tested sample is a fractured crystalline rock with very low permeability, one dimensional advection in the micro channel is coupled with two dimensional matrix diffusion as shown in Figure 1b. The difference between the inlet and outlet is simply due to diffusion ( $D_e$ ) and adsorption ( $K_d$ ) into the rock, and therefore a fitting procedure can be adopted to extract the  $D_e$  and  $K_d$  values.

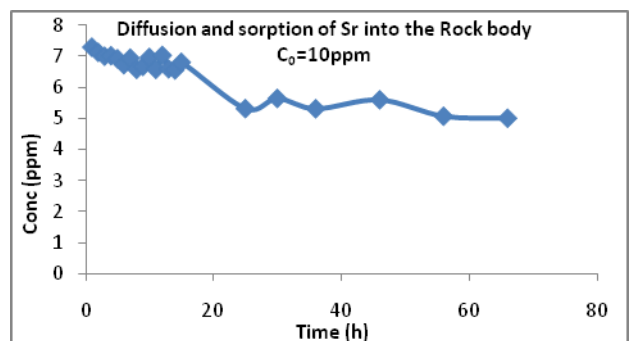
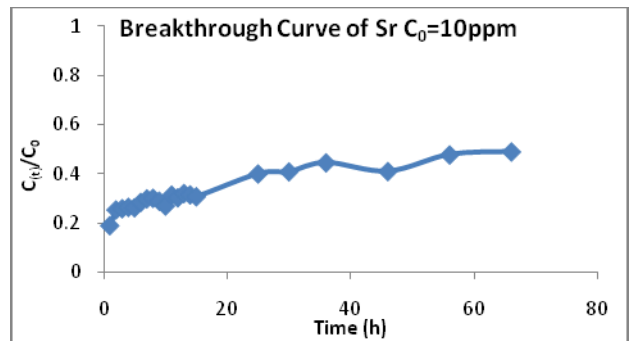
**RESULTS**

In the micro-channel method, the removal of the tracer because of interactions with the solid rock along the flow channel is easily detected by analyzing the outlet concentration of the tracer of interest. Because the tracer is removed from the solution within the channel by matrix diffusion and surface sorption, the outlet concentration will be reduced relative to the inlet. This change in concentration and the shape of the breakthrough curve can be mathematically modeled such that the physical parameters describing diffusion and adsorption may be determined. An independent measurement of the adsorption coefficient is often also done which reduces the degrees of freedom in the fitting regimen. Detection time relies on the flow rate such that the slower the rate, the higher the sensitivity of the analysis. A preliminary experiment was run with Sr, a relatively strongly adsorbing element, at a concentration at 1000 ppm with granite from Cornwall, UK. The breakthrough

curve of Sr (1000 ppm) at the outlet of micro channel is shown in Figure 2. The ordinate shows the Sr concentration at the exit of the bottom channel ( $C_{(t)}$ ) normalized with respect to the inlet concentration ( $C_0$ ). The change of the concentration is driven by solute loss by diffusion into the rock matrix plus adsorption onto the mineral surfaces. From Fig 2, the breakthrough curve does not vary too much over the time of the experiment because adsorption sites on the rock are quickly saturated from the outset of the experiment under such high concentrations. However the outlet concentration does increase slightly over the course of the experiment which could be explained by slow saturation of the few remaining lower affinity adsorption sites in contact with the solution.



**Figure 2** Breakthrough curve of Sr using micro-channel with initial concentration at 1000 ppm



**Figure 3** Breakthrough (a) and diffusion/sorption (b) curve of Sr using micro-channel with initial concentration at 10 ppm

A second experiment was completed at a lower initial Sr concentration of 10 ppm. The

breakthrough curve for this experiment is shown in Figure 3a and exhibits a clear trend; overall the curve indicates that surface sorption and matrix diffusion happen simultaneously in the beginning of the experiment, up to approximately 24 hours. Then the curve becomes asymptotic, suggesting that the surface sorption sites are approaching saturation and that the process of matrix diffusion begins to dominate the system. The term matrix diffusion here not only includes effective diffusion but also sorption within distal pore space (as opposed to adsorption within the channel). Figure 3b indicates absolute Sr concentration lost from solution as a function of time as measured at the outlet from the channel; obviously it is large at the beginning. Figure 3 shows that the asymptote in this experiment is at  $C(t)/C_0=0.5$ , indicating that half of the Sr in the flowing channel is lost into the rock sample.

## CONCLUSION

There are three advantages of the micro-channel method, 1) high sensitivity which is because it is easy to detect the concentration decrease between inlet and outlet, 2) short testing period since it only takes several days to reach steady state, and 3) a simple setup which is easy to handle. Further work will include the numerical modelling to calibrate the breakthrough curves in order to obtain the  $D_e$  and  $K_d$  values. In order to fully constrain the tested element inventory in the near surface of the solid and depth profile within the solid, an analytical regimen is needed. Our detailed approach involves preliminary analysis by Environmental Scanning Electron Microscope (ESEM) to determine grain morphology as well as check whether the tested element has indeed measurably increased in concentration after the reaction. Glancing incidence X-ray Diffraction (XRD) will be used to identify the starting minerals and make surface sensitive measurements of any secondary precipitates that form during the experiments, thereby accounting for solute loss by precipitation as opposed to adsorption or diffusion. Then, chemical surface analysis using techniques such as Proton Induced X-ray Emission (PIXE) or Synchrotron Rapid Scanning X-ray Fluorescence will be employed to accurately quantify the uptake of the tested element by the mineral surface in the micro-reactor experiment. Rutherford Back Scattering (RBS) may be used to further determine the diffusion profile below the surface in order to give a fully constrained concentration depth profile with good elemental resolution.

## REFERENCES

- Bodin, J., F. Delay, et al. (2003). "Solute transport in a single fracture with negligible matrix permeability: 1. Fundamental mechanisms." *Hydrogeology Journal* 11(4): 418-433.
- Byegard J, Johansson H, Skalberg M, Tullborg EL (1998). The interaction of sorbing tracers with different \_sp\_ rock types: sorption and diffusion experiments in the laboratory scale, SKB TR 98-18. Swed Nucl Fuel Waste Manage Co, Stockholm, Sweden, 105 pp
- Cvetkovic V, Selroos JO, Cheng H (1999) Transport of reactive tracers in rock fractures. *J Fluid Mech* 378:335–356
- Freeze RA, Cherry JA (1979) *Groundwater*. Prentice-Hall, Englewood Cliffs, NJ, USA.
- Krauskopf, KB., 1988. *Radioactive waste disposal and geology*. Chapman and Hall, London, UK. 1-24.
- Neretnieks, I., 1980. Diffusion in the rock matrix: An important factor in radionuclide retardation? *Journal of Geophysical Research* 85, 4379–4397.
- Neretnieks, I., 1993. Solute transport in fractured rock --- Application to radionuclide waste Repositories. 39-123. Bear J, Tsang CH, de Marsily G (eds) (1993) *Flow and contaminant transport in fractured rock*. Academic Press, San Diego, CA, USA.
- Noshita, K., et al., "Micro-Flow Channel Probe for Geological Environmental Diagnosis-New Integrated Device for In-situ Measurement of Diffusivity and Sorption Coefficient in Rock Matrix-," Topic D.2, Waste Management Symposia 09, March 1-5, Phoenix, Arizona, 2009.
- Novakowski KS, Bogan JD (1999) A semi-analytical model for the simulation of solute transport in a network of fractures having random orientations. *Int J Numerical Anal Methods Geomech* 23(4):317–333
- Bodin, J., F. Delay, et al. (2003). "Solute transport in a single fracture with negligible matrix permeability: 1. Fundamental