

## Experimental Methods and Development of Models on Diffusion of Nuclides onto Rocks

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### 1. Introduction

In the context of nuclear waste repositories, the rock matrix can act as a barrier against radionuclide migration and matrix diffusion can be an important mechanism for delaying the arrival times to the biosphere. It takes a growing interest whether matrix diffusion is an important retarding and dispersing transport mechanism for solutes carried by groundwater in fractured porous media. It can retard solutes by spreading them from the flowing groundwater into the diluting reservoir of the interconnected pore space of the rock matrix, and providing an increased surface for sorption processes.

Diffusion experiments has been carried in crystalline rocks to determine the diffusivities of some radionuclides either by through-diffusion cells or in-diffusion setups. We'd like to compare the experimental methods and their functions according to sorption properties of species.

### 2. Experiments

Two kinds of experimental setup were designed as through-diffusion type ; one keeps a constant source concentration, the other has a variable source concentration. The experimental setups are separated a cylinder into two blocks by a rock slice as shown Fig.1. The rock disk was fixed in the middle of an acrylate column and sealed with a silicone or epoxy resin. Rock sample was immersed in the groundwater for a month prior to the diffusion experiment. The rock was sampled at the east coast of Korea, which has a porosity of 0.004, the specific surface of 1m<sup>2</sup>/g by BET method, the density of 2.55g/ml, and the cation exchange capacity of 6.8meq/100g. Both sides of the column were filled with the groundwater and the radionuclides as

diffusing species were added in the source side. Tritium and anions were used as nonsorbing tracers, while, strontium, cobalt, cesium, and uranium used as sorbing tracers. The 1 ml of solution was taken from the sampling hole at both sides to measure the concentration change at a certain time interval. When a rock coupon is kept in contact with the solution in the through-diffusion system, radionuclides sorb and diffuse through the rock.

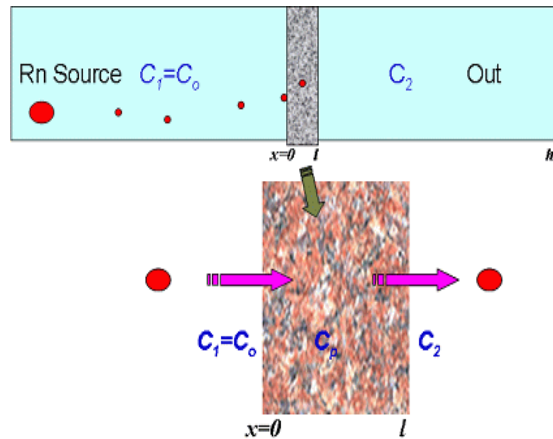


Fig.1 Schematic diagram of the experimental setup

In the constant source concentration, a concentration curve from the through-diffused side can be fitted. When the system is arrived in a steady-state, the following equation can be applied to get the diffusivity.

$$\frac{C_2}{C_0} = \frac{D_e}{lh} t - \frac{lR}{6h}$$

While, in the variable concentration, we can trace the concentration change in the function of time using an unsteady-state diffusion model as follows.

$$\frac{C_2}{C_0} = \frac{1}{2 + \beta} + 2 \sum \frac{(\beta^2 + \phi^2) \exp[-\alpha \phi^2]}{\phi^4 / 4 + 2(1 + \beta)\phi^2}$$

Where,  $\alpha = D_a t / l^2$ ; dimensionless time

$\beta = RA/V$  ; ratio of sorption capacity of the rock to the solution.

### 3. Experimental Results

Because tritium and anions do not sorb on the rock surface, they migrate mainly by pore diffusion. The apparent diffusivity of tritium is obtained about  $8.5 \times 10^{-6} \text{cm}^2/\text{s}$  from the experimental curve. The molecular diffusivity of tritium is  $2.4 \times 10^{-5} \text{cm}^2/\text{s}$  at  $25^\circ\text{C}$ , the geometric factor of the granite can be obtained as 0.35. On the other hand, when the sorbing tracers diffuse into the rock pores, probably the most portion of the solutes sorbs on the pore surface, and some portion of the sorbed solutes desorb and diffuse again, or some of them may migrate on the sorbed phase, which is called the surface diffusion. The apparent diffusivity of cesium is obtained about  $1.5 \times 10^{-7} \text{cm}^2/\text{s}$  from the experimental curve. The measured  $K_d$  value of the granite is about  $800 \text{ml/g}$  in a separated batch test. And the molecular diffusivity of cesium is  $2.0 \times 10^{-5} \text{cm}^2/\text{s}$  at  $25^\circ\text{C}$ , thus the pore diffusivity of cesium is obtained about  $7.2 \times 10^{-6} \text{cm}^2/\text{s}$  and the surface diffusivity of cesium is about  $3.8 \times 10^{-8} \text{cm}^2/\text{s}$ .

To get the diffusivity of the highly sorbing tracers such as  $\text{Cs}^+$  and  $\text{Co}^{+2}$ , it takes more than an year in the constant source concentration system, the steady-state diffusion system, while the variable concentration system, unsteady-state diffusion system, takes less time than the former. Thus, the latter has advantage over the former for the highly sorbing tracers even though it requires a complicate computer simulation to obtain the diffusivity.

### 4. Conclusion

The steady-state diffusion system can be easily used to determine the diffusivity of species. However large volume of source solution is required to maintain the constant concentration. The unsteady-state diffusion system has a simple setup and requires less time to fit the experimental data for sorbing nuclides comparing to the steady-state

system. In the aspect of diffusion mechanism, pore diffusion was found dominant for the nonsorbing nuclides, while for the sorbing ones pore diffusion and surface diffusion occur simultaneously. However, surface diffusion appeared to be dominant in the apparent diffusivity.

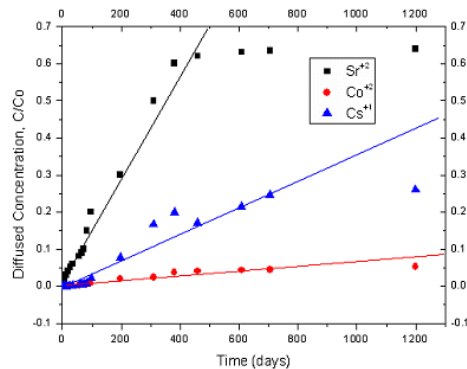


Fig.2 Through-diffusion curve fittings for the tracers

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