

Transient Diffusion of Tracers in Aqueous Phases through Crystalline Rocks : Derivation of an Analytical solution and its Application

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1. Introduction

In order to evaluate matrix-diffusion effects of radionuclides into a rock-mass, most of researchers used through-diffusion cells assuming source concentrations in a source cell are kept constant with time[1,2]. To satisfy this assumption for highly sorbing tracers, a larger solution reservoir of the tracer is required. Diffusivities of nuclides can be determined from a curve fitting for the diffused concentrations as a function of time with a steady-state diffusion model. When it is allowed the change of the concentration of the nuclides in the source cell, an experimental setup can be established with a simple structure and maintained easily. However, there is not general analytical solutions for such transiently decreasing cases in the source concentration. This study intends to find an analytical solution for an unsteady-state diffusion system and apply it to experimental results of through-diffusion.

2. Unsteady-state diffusion model

When radionuclides move through rock pores in aqueous phase as well as in sorbed phases on a rock surface, the rate of concentration change in the rock can be described as

$$e \frac{\partial C_p}{\partial t} + (1-e)\rho \frac{\partial q}{\partial t} = eD_p \frac{\partial^2 C_p}{\partial x^2} + (1-e)\rho D_s \frac{\partial^2 q}{\partial x^2}$$

It can be reduced to

$$R \frac{\partial C_p}{\partial t} = D_a \frac{\partial^2 C_p}{\partial x^2}$$

Initial and boundary conditions are

$$\begin{aligned} C_1(t=0) &= C_0 & C_2(t=0) &= 0 \\ C_p(x,0) &= 0, \quad 0 < x < 1 & C_p(0,t) &= 0, \quad 0 < x < 1 & C_p(1,t) &= C_2 \\ V \frac{dC_2}{dt} &= -\varepsilon A D_p - (1-\varepsilon) A \rho D_s \frac{\partial q}{\partial x} \Big|_{x=1} \end{aligned}$$

The analytical solution can be obtained by Laplace transform 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, $\tau = D_a t / l^2$; dimensionless time, $\beta = RA / V$; ratio of sorption capacity of the rock to the solution.

3. Experimental

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 1m²/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.2 shows the concentration change of a highly sorbing tracer as a function of time. After 10⁴ hours, the

concentrations at both sides of the diffusion cell show a trend to approach toward one concentration point, that is, a diffusive equilibrium. The unsteady-state diffusion model is applied to analyze these diffusion curves. At the initial stage of the diffusion, diffusing species are contacted only at the surface of the rock. As diffusion time goes on, contacting surface area and sorbed solutes are increased. When sorption and diffusion occur in the whole rock body, the sorption phase is going to an equilibrium point. Thus a kinetic sorption parameter is required, $K_s(t) = \frac{K_d * t}{K_s + t}$

Where K_s is a constant equal to the time when $Kt=Kd/2$. Kt describes that sorption of radionuclides on the whole rock body increases with diffusing time before the equilibrium state. Then the overall sorption and diffusion process coincides with the unsteady-state diffusion model. The simulated curve fitted well with the experimental data in Fig.2. The calculated D_a is $3.8 \times 10^{-12} \text{m}^2/\text{s}$.

4. Conclusion

An analytical solution is derived and applied for an unsteady-state diffusion system successfully. That 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. And surface diffusion plays an important role in diffusive transport.

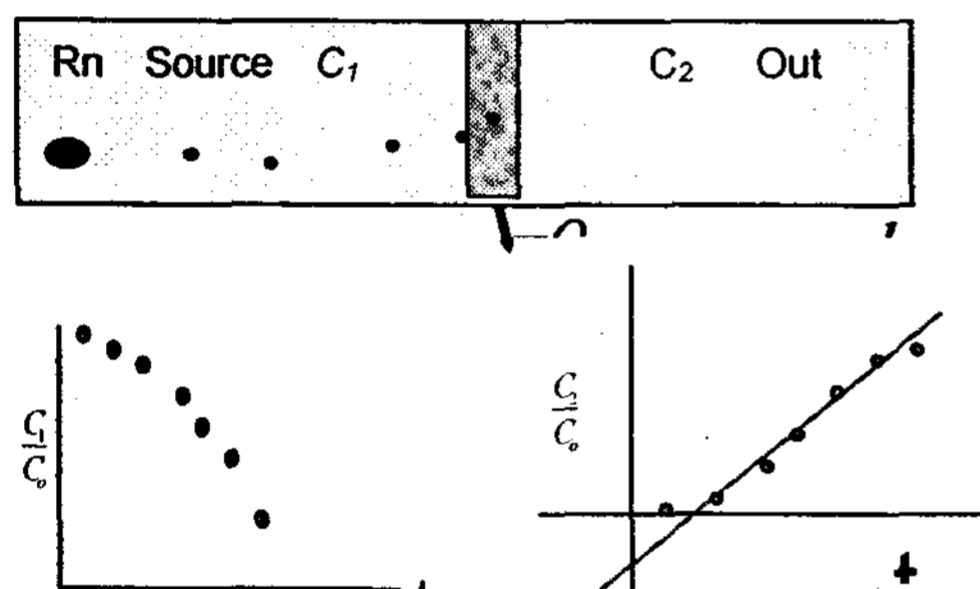


Fig.1 Conceptual diagram of an unsteady-state diffusion for the tracers

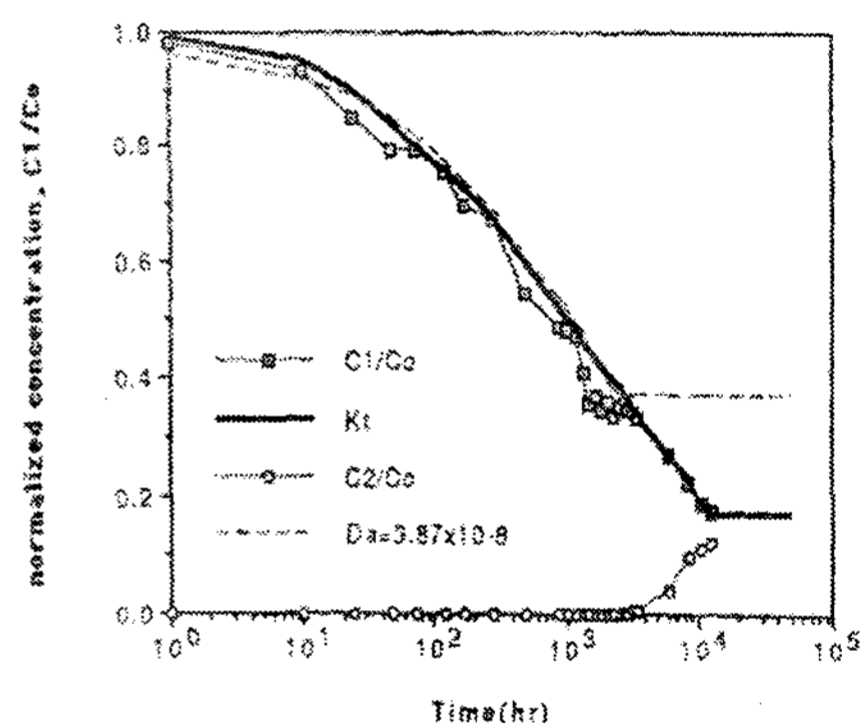


Fig.2 Through-diffusion curve fittings for the tracers

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