

**Influences of Temperature on Permeability Changes of Flow-paths Altered by Highly Alkaline Ca-rich Groundwater – 15192**

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**ABSTRACT**

Fractures (or cracks) in host rock around the geological repository are considered as main flow-paths for the migration of radionuclides. Such fractures would be altered by the alkaline components (Ca, Na, K) leaching from cementitious materials for the construction of the repository. While silicate minerals in fractures are dissolved by highly alkaline groundwater, secondary minerals would deposit on the surface of fractures because of the reaction between the alkaline components and silicate species. The authors' previous study showed the generation of CSH-gel and the clogging of micro flow-path under the condition of Ca-rich and high pH by flow experiments. The present study examined the permeability changes with temperature in micro flow-path flowing highly alkaline Ca-rich solution, considering temperature at the depth of geological disposal system. For the simulation of micro flow-path such as fractures, "micro flow-cell," which nipped a thin Teflon sheet with a slit between granite chip and Teflon basement, were used for the experiments. Highly alkaline Ca-rich solution (pH>12 and 8.5 mM Ca(OH)<sub>2</sub>) were injected into micro flow-cell with 2.0 ml/h of flow rate under the given temperature conditions (278 K, 296 K or 313 K). As a result, the permeability became lower with the increase in temperature. In addition, the deposition rates of CSH-gel became larger with the increase in temperature, and the activation energy was estimated to be 32.0 kJ/mol. These results suggest that flow-paths around the geological repository would undergo the clogging with CSH-gel in a shorter time-period under a condition of higher temperature.

**INTRODUCTION**

For the geological disposal system in Japan, crystalline rocks, assuming mainly granite, are expected as the host rock of the natural barrier around the repository [1]. Fractures (or cracks) in the host rock around the repository are considered as main flow-paths for the migration of radionuclides. The physical and chemical properties of these flow-paths are often assumed to be unchanged in the assessment of radionuclides migration. However, the condition of the natural barrier including host rock would be altered by various factors caused from the construction of the repository. Above all, a large amount of cementitious materials of the repository alter groundwater from 8 to 13 in pH and release the alkaline components such as calcium ions, sodium ions and potassium ions [2]. This highly alkaline groundwater dissolves silicate minerals in flow-paths due to the increase in the solubility of silicic acid [3]. Then, by the reaction of calcium ions and silicic acid under a high pH condition, calcium-silicate-hydrate (CSH-gel) deposits as a secondary mineral on the surface of flow-paths. CSH-gel may not only adsorb radionuclides but also clog the flow paths [4]. Such effects of CSH-gel might cause the retardation effect for the migration of radionuclides.

In the previous study, the authors have discussed on the permeability changes of flow-paths due to contact with highly alkaline Ca-rich solution ( $\text{pH} > 12$ ) by using a flow-path simulated by nipping a thin Teflon sheet with a slit between granite chip and Teflon basement [5]. (Hereinafter, this micro flow system is referred to as micro flow-cell.) The experimental results showed the remarkable changes of the permeability due to the partial clogging with the heterogeneous deposition of CSH-gel on the surface of granite-chip under an isothermal condition (room temperature). The present study focused on the influence of temperature on the permeability through micro flow-paths with the deposition of CSH-gel. Generally, the temperature of groundwater increase as the depth from the surface becomes deeper (e.g. 3 K per 100 m). Considering temperature changes at the depth of geological disposal system is very important because the temperature changes greatly affect the chemical reactions, such as dissolution, deposition and precipitation.

## EXPERIMENTAL

The main experimental procedures are the same as the authors' previous work [5,6]. In the experiments, the micro flow-cell was prepared with Teflon sheet of  $80 \mu\text{m}$  in thickness contacting a granite-chip as shown in Fig. 1. The Teflon sheet had a slit of 5 mm in width and 60 mm in length. The injection flow rate was set to 2.0 ml/h by using the constant flow-rate pump. The injection solution was 8.5 mM  $\text{Ca}(\text{OH})_2$  solution adjusted to pH 12.2 to 12.5 with NaOH solution. The temperature was set to 278 K, 296 K or 313 K by submerging the micro flow-cell into a thermostat water bath. For the estimation of the over-all permeability of the micro flow-cell, the pressure difference between the inlet and the outlet was monitored by a pressure gauge. In addition, apparent deposition rate constants were estimated based on the permeability changes with time in the same way as the previous studies [5], as described later. In order to avoid the formation of calcium carbonate, the injection solution was purged with nitrogen gas. Besides, nitrogen gas was continuously passed through the fraction collector attached at the outlet. The concentrations of Ca and Si eluted from outlet were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The pH value at outlet was also measured.

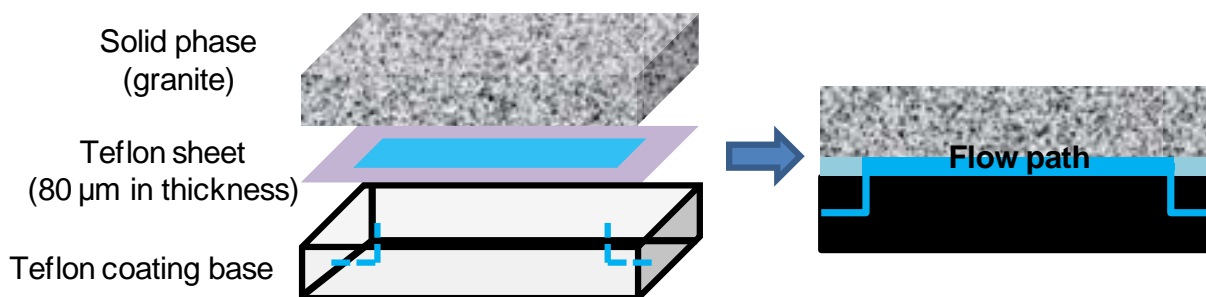


Fig. 1. Illustration of micro flow-cell [5].

### Measurement of Permeability

In the same way as the previous study [5], the values of permeability were determined. Based on Darcy's law, the relation of the pressure differential and the permeability ( $\text{m}^2$ ),  $k$ , can be described by

$$v = \frac{k}{\mu} \frac{p_{in} - p_{out}}{x_1}, \quad (\Delta p \equiv p_{in} - p_{out}), \quad (1)$$

where  $v$  is Darcy's fluid flow velocity (m/s),  $\mu$  is the fluid viscosity (Pa·s),  $p$  is the pressure (Pa),  $x_1$  is the length of the micro flow-cell along flow direction (m), and the subscripts, in and out, mean the inlet and outlet of the micro flow-cell, respectively. Besides, the volume flow rate,  $Q$  (m<sup>3</sup>/s), is given by

$$Q = wbv, \quad (2)$$

where  $w$  is the width of the slit in the micro flow-cell (m),  $b$  is the aperture of flow-path (m). Thus,  $wb$  means a cross section area (m<sup>2</sup>). On the other hand, the permeability of parallel flat board layer is generally approximated by  $k = b^2/12$  [7]. Using equations (1) and (2),  $b$  can be estimated by

$$b = \left( \frac{12\mu Q x_1}{w\Delta p} \right)^{\frac{1}{3}}. \quad (3)$$

Furthermore, from the estimated  $b$  and  $k = b^2/12$ , we can determine the permeability  $k$ .

### Evaluation of Deposition Rate of CSH-gel

The deposition rates of CSH-gel in the micro flow-cell were evaluated [5]. In these experiments, it was confirmed that the concentration of Ca ions and the pH, which were enough high for the formation of CSH-gel, hardly changed between inlet and outlet of the micro flow-cell. These mean the apparent deposition rate constants can be evaluated by assuming the one-order reaction. The rate constant (m/s),  $k_R$ , is described by

$$\rho_M (b_0 - b) = \int_0^t k_R c dt, \quad (4)$$

where  $\rho_M$  is the density of CSH (mol/m<sup>3</sup>),  $b_0$  is the initial aperture of flow-path (m),  $b$  is the aperture of flow path (m) at time  $t$  (s), and  $c$  is approximately equal to the concentration of Ca ions at the inlet (mol/dm<sup>3</sup>). Here,  $b = b_0$  when  $t = 0$ . When  $c$  and  $k_R$  are constant, Eq. (4) yields

$$k_R = \frac{\rho_s (b_0 - b)}{ct}. \quad (5)$$

The change in the aperture of flow-path is reflected to the change in the permeability. As Eq. (5) is rewritten with  $k = b^2/12$  and  $K = k/k_0$  ( $k_0$  is the initial permeability), Eq. (6) is obtained.

$$K = \left(1 - \frac{k_R c}{\rho_s b_0} t\right)^2. \quad \therefore \sqrt{K} = 1 - \frac{k_R c}{\rho_s b_0} t. \quad (6)$$

Eq. (6) means that the apparent deposition rate constant,  $k_R$ , of CSH-gel can be evaluated from the time dependency of the permeability change.

**RESULTS AND DISCUSSION**

Fig.2 shows the temperature dependencies of the permeability change. As shown in Fig. 2, the permeability in the range of temperature gradually became low with time due to the deposition of CSH-gel. Furthermore, with the increase in temperature, the permeability became lower, and the gradient of the permeability change became larger. That is, the deposition rates of CSH-gel were estimated to be larger with the increase in temperature as described later. The reasons may be as follows: under the condition of higher temperature, the formation of CSH-gel becomes faster, and the supply rate of silicic acid from the surface of granite chip increases because the solubility of silicic acid becomes higher. These results suggest that the flow-paths around the repository would undergo the clogging with CSH-gel in a shorter time-period under a condition of higher temperature.

Fig. 3 shows the time dependencies of the pH and the concentration of Ca and Si ions at the outlet of micro flow-cell. In these experiments, Si ions could hardly detect at the outlet. All of silicic acid which dissolves from granite under the high pH condition would be consumed for the formation of CSH-gel. The concentration of Ca ions and pH at the outlet were kept the condition of the injected solution. That is, the apparent deposition rate constants of CSH-gel can be evaluated by the calculation procedure as mentioned above. The evaluated deposition rate constants are shown in Fig. 4. The deposition rate constants became larger with increment of temperature. Through the Arrhenius plot as a function of apparent deposition rate constants and temperature in Fig. 4, the apparent activation energy for the deposition of CSH-gel in micro flow-cell was estimated to be 32.0 kJ/mol. For example, the activation energy for the dissolution of quartz, which is the main mineral in granite (containing 40 wt% or more [8]), has been reported 45.5 kJ/mol [9]. This activation energy for the dissolution of quartz are slightly larger than that for the deposition of CSH-gel in this study.

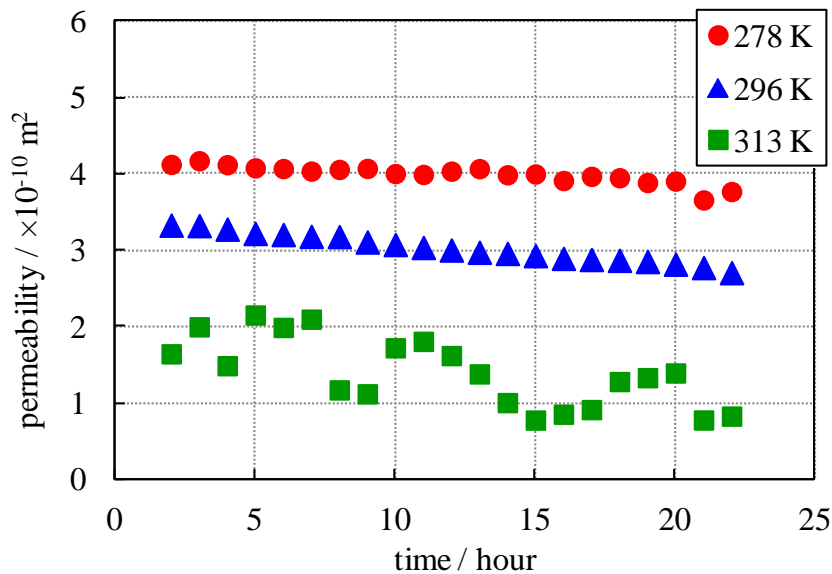


Fig. 2. Temperature dependencies of the permeability change.

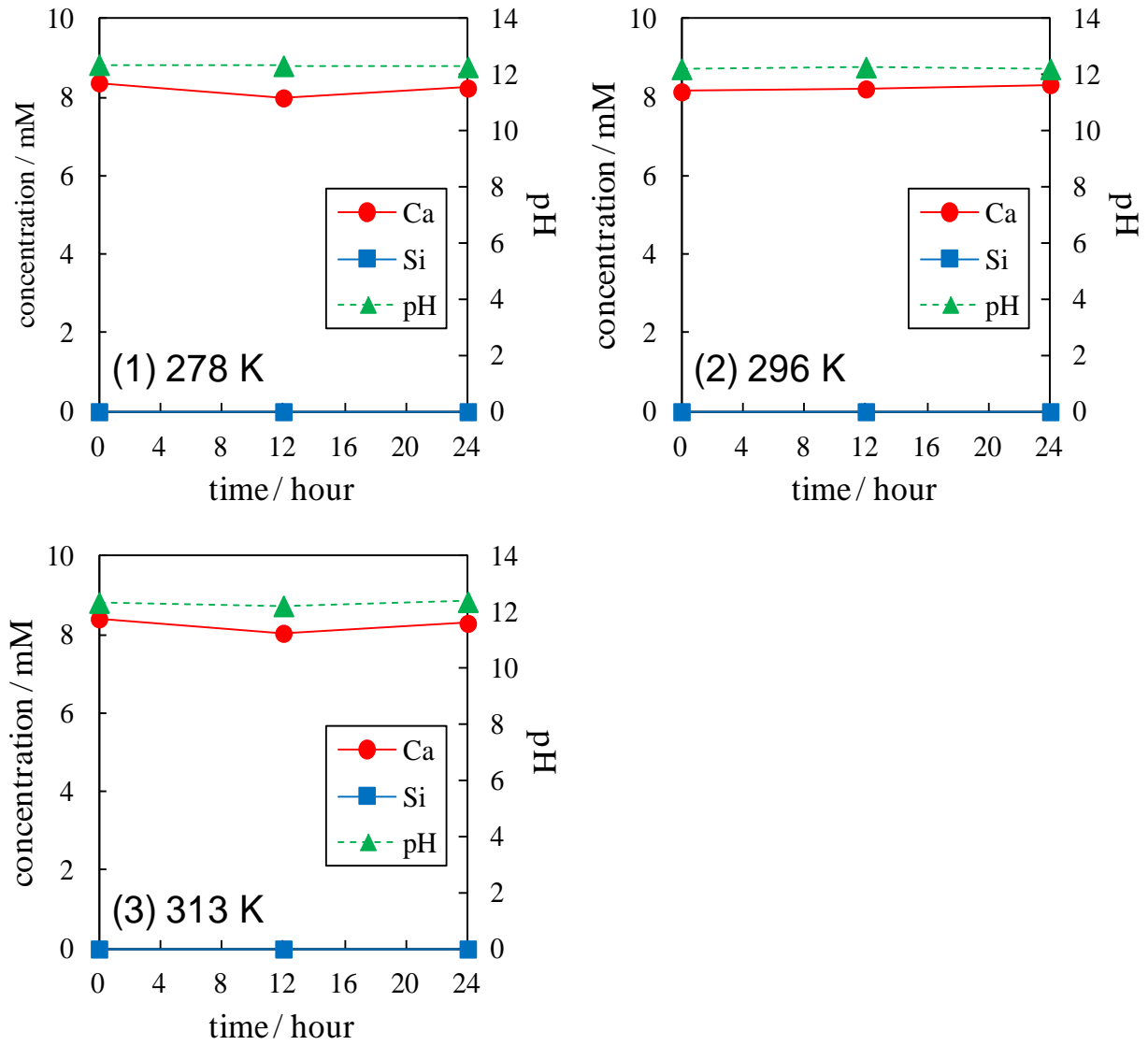


Fig. 3. pH and concentration of Ca and Si at outlet of micro flow-cell.

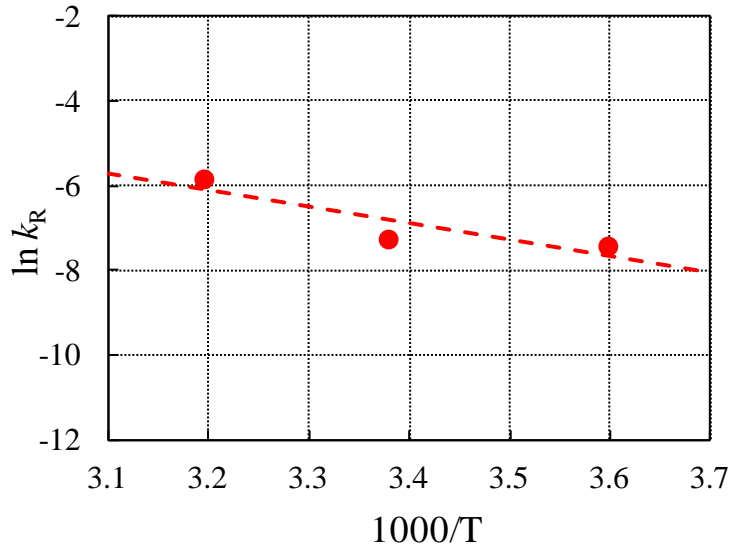


Fig. 4. Arrhenius plot of the deposition rates.

When the deposition reaction rate of CSH-gel are controlled by the dissolution rate of silicate minerals in granite, their activation energies are supposed to show the almost same values. On the other hand, the previous study has reported that the apparent deposition rate constants of CSH-gel decreased with the increment of flow rate through the micro flow-cell [5]. The decrease in the deposition rate constant was due to the slight outflow of CSH-gel from the micro flow-cell with increment of the flow rate. Therefore, these results in this study suggest that the deposition of CSH-gel was controlled not only by the supply of silicic acid from quartz (and other similar minerals) in granite but also the migration of suspended CSH-gel (mass transfer) through micro flow-path in the natural barrier of geological disposal system.

## CONCLUSIONS

This study discussed the influence of temperature on the permeability changes of flow-paths altered by a highly alkaline Ca-rich solution. In the experimental results, the permeability through micro flow-cell became lower with the increase in temperature. These results suggested the acceleration of CSH-gel formation with the increase in the supply rate of silicic acid. Furthermore, the evaluated deposition rate constants became larger with the increase in temperature, although the suspension of CSH-gel might flow out of the micro flow system. These mean that the clogging with CSH-gel in fracture of granite would be accelerated under a relatively higher temperature condition such as in the geological repository.

Cementitious materials for the construction greatly alter the chemical and physical properties around the repository, and may degrade the retardation effect for radionuclides in the natural barrier. However, on the other hand, some interactions of cementitious components and silicate species in the natural barrier can contribute the immobilization of radionuclides as shown in this study. The dependence of CSH gel formation on temperature also might be a key factor for more realistic safety assessments considering the influences on the repository system caused by the use of cementitious materials.

## REFERENCES

1. JNC (Japan Nuclear Cycle development institute), “H12 Project to Establish the Scientific and Technical Basis for HLW Disposal in Japan, Supporting Report I, Geological Environment in Japan,” JNC-TN1400-99-021 (1999).
2. A. ATKINSON, “The Time Dependence of pH within a Repository for Radioactive Waste Disposal,” AERE R 11777, UKAEA (1985).
3. W. STUMN and J.J. MORGAN, *Aquatic Chemistry 3rd ed.*, John Wiley & Sons, New York (1996).
4. H. SHINMURA, Y. NIIBORI and H. MIMURA, “Fundamental Study on Temperature Dependence of Deposition Rate of Silicic Acid,” Proc. of WM2013, Paper No. 13270 (2013).
5. D. KURATA, T. CHIDA, Y. NIIBORI and H. MIMURA, “Estimation of Permeability Changes due to Contact with Highly Alkaline Ca-rich Solution by Micro Flow-Cell of Granite Chip,” Proc. of WM2014, Paper No. 14094 (2014).
6. Y. Niibori, K. Komatsu and H. Mimura, “Deposition of Calcium-Silicate-Hydrate Gel on Rough Surface of Granite from Calcium-rich Highly Alkaline Plume,” Scientific Basis for Nuclear Waste Management XXXV (MRS Proc.), **1475**, 349-354 (2012).
7. A.P. Oron and B. Berkowitz, “Flow in rock fractures: The local cubic law assumption reexamined,” *Water Resources Research*, **34**(11), 2811-2825 (1998).
8. Y. Niibori, H. Futamata and H. Mimura, “Evaluation of Radionuclide Transport in Rock Matrix with Heterogeneous Distribution of Retardation Coefficient,” Proceedings of 16<sup>th</sup> Pacific Basin Nuclear Conference (16PBNC), P16P1074, 1-6 (2008).
9. P.M. Dove, “Kinetic and thermodynamic controls on silica reactivity in weathering environments, *Reviews in Mineralogy Volume 31*,” Mineralogical Society of America, Washington, D.C, 235-290 (1995).

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