Influence of Calcium Concentration on Permeability Changes in Flow-paths Altered by Highly Alkaline Groundwater – 17129

Ryo Tashiro *, Daiki Kurata *, Yuichi Niibori *, Taiji Chida *
* Tohoku University

ABSTRACT

Groundwater around the geological repository of HLW is altered to the highly alkaline and Ca-rich condition by the constituents leaching from cementitious materials. Under such condition, the formation of CSH will affect the migration of radionuclides with the change in the hydraulic and chemical properties of the fracture (micro flow-path) in the host rock. In particular, the clogging effect with the deposition of CSH in the flow path the may contribute the retardation of radionuclide migration. In this study, the influence of Ca concentration on such clogging effect in the micro flow-path under the highly alkaline condition was examined by estimating the permeability changes with the deposition of CSH. In the experiment, the micro fractures in host rock were simulated by the micro flow-cell nipping the Teflon sheet (80 μm of thickness) between a granite chip and Teflon basement. The flow experiment was conducted by continuously injecting Ca solution to the micro flow-cell with constant flow rate. The concentrations of Ca ions for the injection solution were set in the range from 0 to 7.5 mM, and the value of pH was 12.5. As a result, under all conditions of Ca concentrations, the permeability in the flow path decreased to the range of 1.0×10^{-10} to 2.0×10^{-10} m^2 with the deposition of CSH. Besides, such decreased permeability was almost constant with increasing and decreasing periodically. Such increase and decrease in the permeability will be caused by the deposition and outflow of CSH formed in the flow path. In other words, because CSH is stable in pH higher than at least 10, under the condition with no man-made outlet such as real underground around the repository of radioactive waste, most CSH might clog through the flow-paths in the spatial range where pH exceeds at least 10, contributing the retardation effect of the migration of radionuclides released from the repository.

INTRODUCTION

Geological disposal of high-level radioactive waste contains and confines radionuclides with a multi-barrier system consisting of multiple engineered barriers and natural barriers. The migration of radionuclides leaching into groundwater from vitrified wastes is limited by many retardation effects of these barriers, such as the sorption of radionuclides, the low permeability, low solubility, and so on until the radioactivity of the wastes decays enough not to affect the human accessible environment. However, these barrier effects may be altered or degraded with the environmental conditions around the repository. The influence of cementitious materials on the barriers is one of the most important factors for the safety assessment of geological disposal facilities. A large amount of cementitious materials will be used for the construction of the geological disposal facility because its underground facility in Japan requires several square kilometers size below water table. These cementitious materials alter the groundwater around the

repository to the highly alkaline condition (pH≈13) by leaching the alkaline components such as calcium (Ca), sodium (Na) and potassium (K) ions [1]. Under such a condition, calcium silicate hydrate (CSH) will form and deposit on the surface of solid phase, as a secondary mineral in the natural barrier near the repository, due to the reaction of Ca ions and silicic acid [2]. Here, the silicic acid is leached from silicate minerals in the host rock under the high pH condition. With the formation of CSH, the migration of radionuclides may be retarded by the sorption on CSH and the clogging with the deposition of CSH in the flow-path (cracks of the host rock). In particular, this study focused on the clogging effect in the flow-path with the formation of CSH because the change of the flow condition directly affects the migration of radionuclides. The authors' previous study reported that the deposition of CSH under the Ca-rich condition ($[Ca^{2+}]$=8.5 mM) can clog the micro flow paths on granite surface [3]. However, the concentration of Ca ions in groundwater around disposal site will be not homogeneous, and gradually change with the leaching of the alkaline plume for a long period [4]. Obviously, the amount of CSH formed in the flow-paths will significantly depend on the concentration of Ca ions. Therefore, in this study, the influence of the Ca concentration on the clogging effect with the formation of CSH in the micro flow-path was examined.

METHODS

Experimental

The experimental procedures were followed the authors' previous studies [5].In the flow experiment, the micro fractures in host rock were simulated by the micro flow-cell nipping the Teflon sheet of 80 μm in thickness with a slit of 5 mm × 60 mm between a granite chip and Teflon basement. Such flow experiments using the micro-flow cell were also reported in some previous studies [6,7]. This thickness was referred to the width of the fracture in the host rock applying for the present assessment in Japan [8]. The surface of the granite chip was ground by an abrasive paper (#2000: 7.9 μm of particle diameter, SiC grinding powder). The schematic view of the experimental device and the structure of a micro flow-cell were shown in Fig. 1 and Fig. 2, respectively. The concentrations of Ca ions for the injection solution were set in the range from 0 to 7.5 mM. The pH in the injection solution was adjusted to 12.5 with a NaOH solution. The flow rate was fixed to 1.0 ml/h with the constant flow-rate pump at a room temperature (298 K). The permeability in the micro flow-path was estimated by measuring the pressure the inlet of the micro flow-cell as described later. The concentrations of Ca and Si outflowed at the outlet of the micro flow-cell were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, SPS7800, Hitachi High-Tech Science Corporation) without filtration treatments. (No solid substances were visually confirmed.) The alteration in the surface of granite was observed by digital micro scope (DMS, VHX-5000, KEYENCE Corporation).
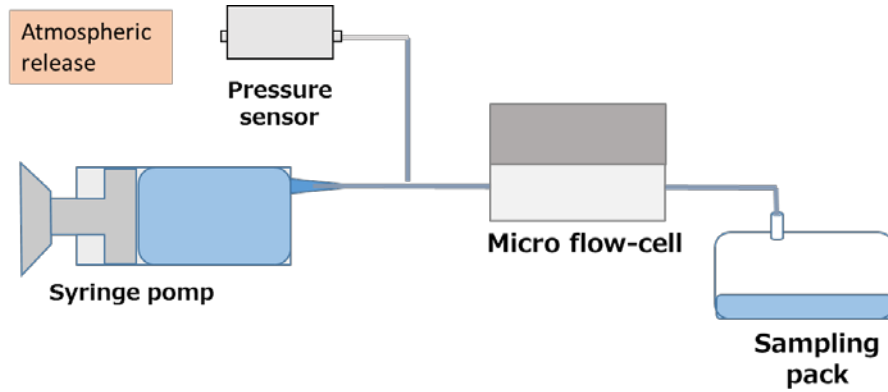
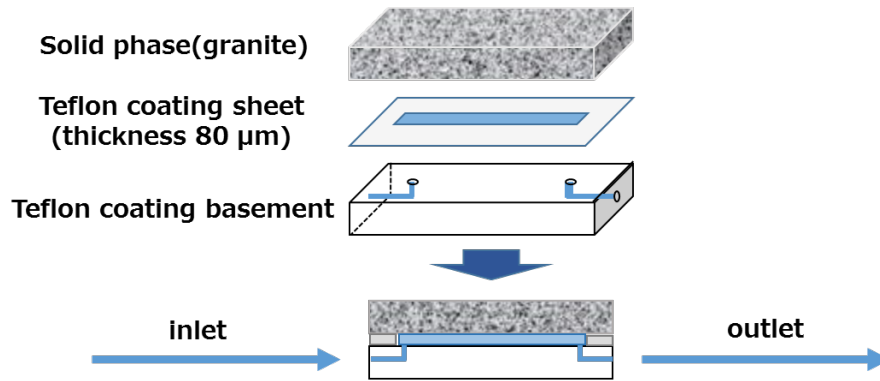Fig. 1 Schematic view of the experimental device.

Fig. 2 Structure of micro flow-cell.

Estimation of permeability
In this study, the permeability was calculated from the pressure change in the flow experiment by referring to the authors' previous work [3]. Fig. 3 shows the illustration of the flow path used in the experiments. In Fig .3, x_1 is the length of flow direction [m], w is the width [m], b is the aperture [m] of the flow path, and bw (=A) means the cross section area [m^2]. The permeability can be described by Eq. (1), based on Darcy's Law.

$$v = \frac{k}{\mu} \frac{\Delta p}{x_1},$$ (1)

where v is Darcy's fluid flow velocity [m/s], k is the permeability [m^2], μ is the viscosity coefficient [Pa·s], and Δp is the pressure difference [Pa]. The volume flow rate, Q [m^3/s], is given as

$$Q = vA = vbw$$. (2)

Besides, Oron & Berkowitz [9] reported that the permeability in the parallel flat board layer as shown in Fig. 5 is can be approximated by

$$k = \frac{b^2}{12}$$. (3)

This study measured pressure difference between the inlet and the outlet, and evaluated the permeability, k, using Eqs. (1) and (2) under the constant flow rate condition (i.e., Q is constant). Then, using Eq. (3), the effective aperture, b, of the flow path was estimated. The viscosity coefficient of fluid, μ, is given as 1.00×10^{-3} Pa·s because the experiments were conducted in constant room temperature (298 K).
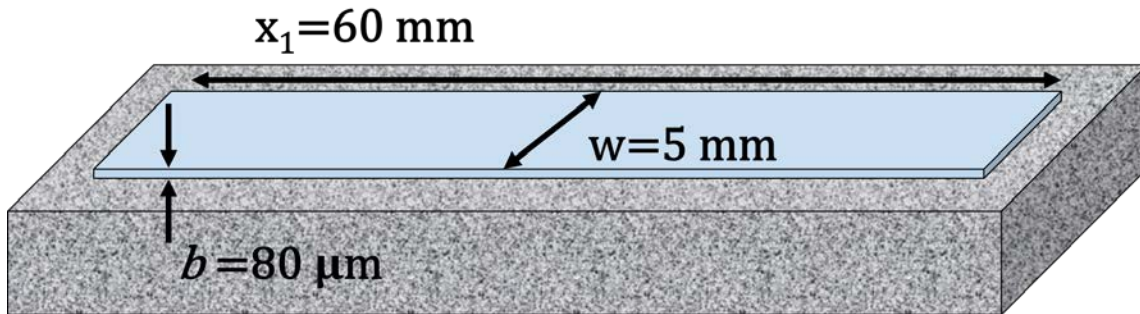

x_1=60 mm

w=5 mm

b=80 μm

Fig.3 Illustration of the flow path in the flow experiment.

RESULTS and DISCUSSION
Change of Permeability and Formation of CSH

Figs. 4-7 show the change of the permeability in the flow experiment for each condition of Ca concentration. Besides, Table 1 shows the concentrations of Ca and Si in the effluent collected to the sampling bag in Fig. 2, comparing with those in the injected solution. In the table, "before" means the concentrations in the solution injected to the flow cell, and "after" means those in the solution eluted from the flow cell. The concentrations of Ca and Si in the effluent includes not only ions but also some invisible species such as micro particles of CSH.
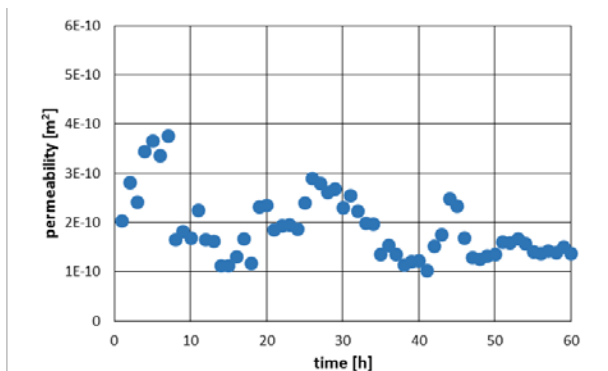

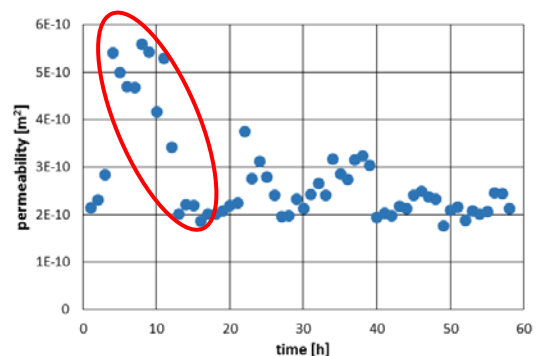Fig. 4   Change of permeability.

(Ca: 0 mM)

Fig. 5   Change of permeability.
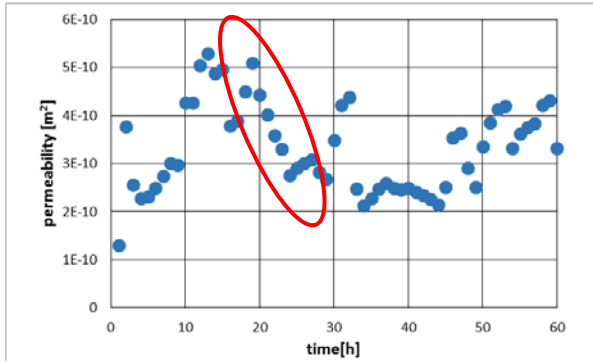
(Ca: 2.5 mM)

Fig. 6 Change of permeability.
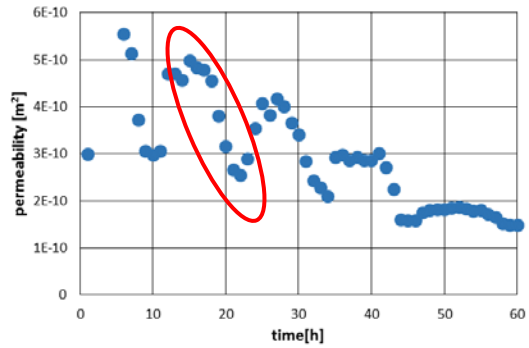
(Ca: 6.4 mM)

Fig. 7 Change of permeability.

(Ca: 7.5 mM)

Table 1   Comparison of the concentration of Ca and Si in the injection solution (=before) and the effluent (=after).

	Ca[mM]	Si[μM]
before	0.00	-
after	0.01	3.63
before	0.31	-
after	0.17	30.47
before	2.51	-
after	2.13	29.90
before	3.80	-
after	2.93	34.18
before	5.06	-
after	4.63	29.19
before	6.44	-
after	5.47	34.18
before	7.51	-
after	7.34	38.34

As shown in Figs. 4-7, under the all injection conditions of Ca ions, the permeability began to decrease in the range of about 10 to 20 hours of the injection time, and gradually dropped to the range of 1.0×10^{-10} to 2.0×10^{-10} m^2 with increasing and decreasing repeatedly. This decrease in the permeability means the micro flow-path is narrowed and clogged by the deposition of CSH with injecting the highly alkaline solution containing Ca ions. This is harmonic to the decrease in the concentration of Ca shown in Table 1. On the other hand, the concentration of Si in the effluent indicates the outflow of CSH because soluble silicic acid rapidly forms CSH with Ca ions under the highly alkaline and Ca-rich condition.

Fig. 8 shows the change of the amount of Si in the effluent with time. The gradual increase in the amount of Si shown in Fig. 8 means the continuous outflow of CSH from the micro flow-cell. Furthermore, Fig. 9 is the relation of Si and Ca in the effluent based on the values in Table 1. The concentration of Si in the effluent became larger up to about 0.3 mM of Ca concentration, and kept constant for the condition of the higher concentration of Ca. These changes in the amount of Si in the effluent suggest that, while the flushed CSH increases with continuously forming CSH, the formation of CSH is limited by the amount of Si dissolved from the granite. Therefore, the constant permeability (in the range of 1.0×10^{-10} to 2.0×10^{-10} m^2) with increasing and decreasing periodically will be caused by CSH deposition balanced to the eluted CSH with the increase of the flow pressure in the micro flow-cell.
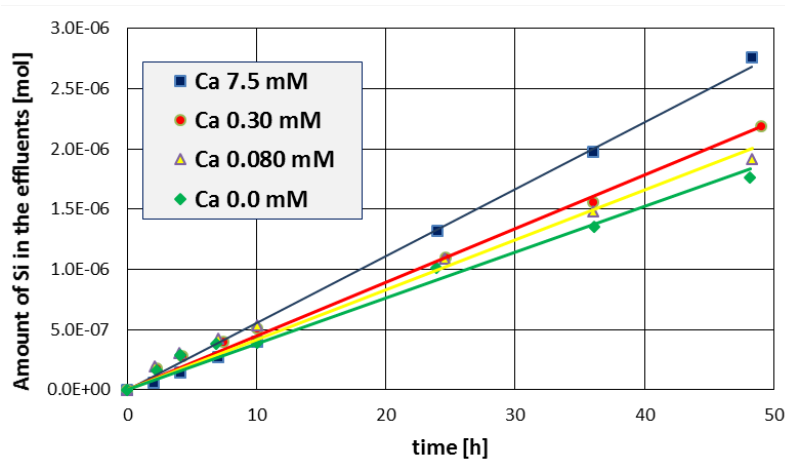

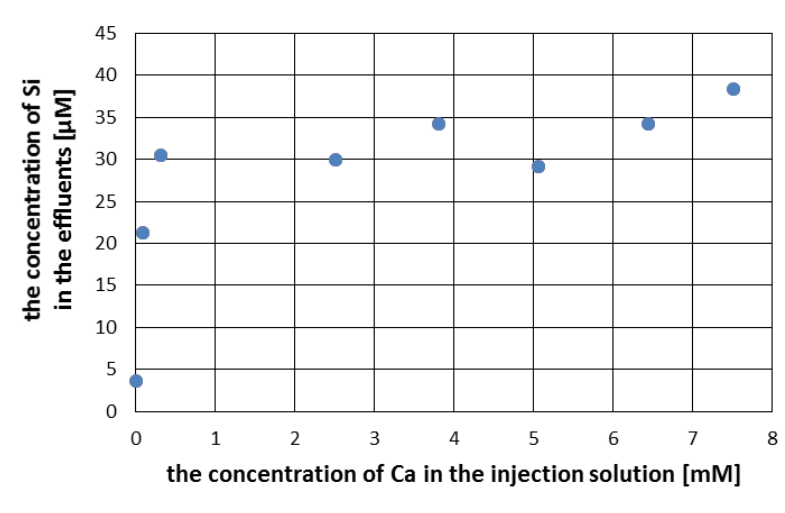Fig. 8 Amount of Si in the effluents for each experiment.

Fig. 9 Relation of the concentration of Si in the effluents to the concentration of Ca in the injection solution for each experiment.

Alteration of Granite Surface
Figs. 10 and 11 show the surface of the flow path in the micro flow-cell observed by DMS. Comparing Fig. 10 to Fig. 11 in the parts of the red circle, the dissolution of white minerals such as quartz was observed. Besides, the deposition of white minerals (probably CSH) covered biotite, as observed at the blue circle in Fig. 11. These results suggest that the dissolution of silicate minerals and the deposition of CSH on the surface of the solid phase will heterogeneously occur at the same time in the flow-paths with injecting the highly alkaline Ca-rich solution.
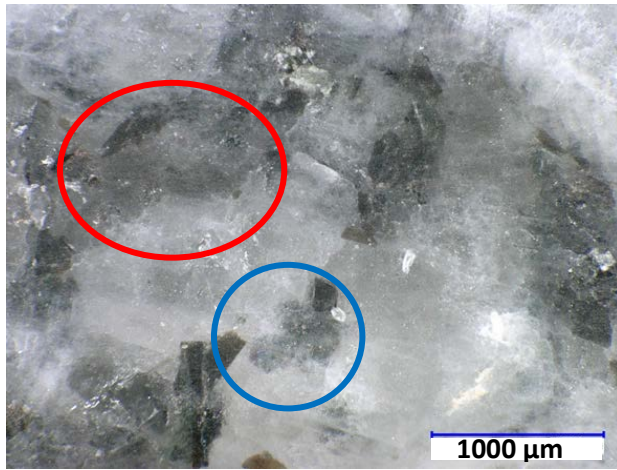

Fig. 10 Granite surface.
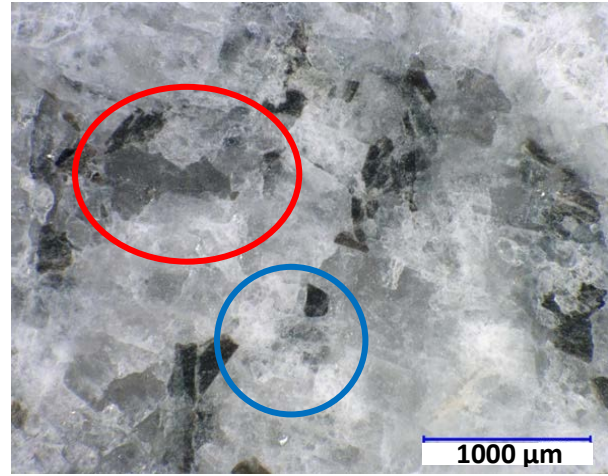(before experiment)

Fig. 11 Granite surface.
(after experiment)

Estimation of Deposition Rate and Outflow Rate
Here, the deposition rate and the outflow rate of CSH were calculated from the experimental result. In this study, the deposition rate of CSH on the surface of the flow path was calculated from the change of the effective aperture defined by Eq. (3). And, the outflow rate was estimated by the amount of Si in the effluent. The calculation procedure is as follows.

According to the experimental conditions, the pH and the concentration of Ca ions were high enough to form and deposit CSH in the flow-paths. Thus, by assuming the one-order reaction for the formation of CSH, the relation between the change in the effective aperture, b_t, of the micro flow-path with time and the apparent deposition rate constant is given as

$$\rho_s s(b_0 - b_t) = \int_0^t s k_R c_{in} dt \quad , \tag{4}$$

$$b_t = b_0 - \frac{k_R c_{in}}{\rho_s} t \quad , \tag{5}$$

where C_{in} is the concentration of Ca ions [mol/m^3], ρ_s is the density of CSH [mol/m^3], b_0 is the initial aperture [m], t is the time [s], k_R is the apparent deposition rate constant [m/s], and s is the specific surface area of solid phase

[m^2]. On the other, the amount of Si in the effluent is related to the outflow amount of CSH as described above. The outflow rate of CSH is expressed as follows:

$$\mu_{CSH} = \mu_{Si} = QC_{si} \quad , \tag{6}$$

where μ_{Si} and μ_{CSH} are the outflow rates of Si and CSH, Q is the flow rate, C_{Si} is the concentration of Si in the effluent.

Fig. 12 shows the change in the effective aperture, b_t, in the flow path with time calculated from the permeability by Eq.(3) for 7.5 mM of Ca concentration. The deposition rates of CSH were calculated from the slope of the decrease in the aperture by Eq. (5). For the estimation of the deposition rates, the slopes for the range from 50 μm to 80 μm of the aperture, which is equivalent to the range from 2.0×10^{-10} to 5.0×10^{-10} of the permeability, were used as shown in Fig. 12, because it was thought that the apparent deposition rate including the flash-out of CSH depends on the flow pressure and the fluid velocity. The flow pressure and the fluid velocity both under the condition of the smaller aperture (<50 μm) apparently become high in comparison with those in the range from 50 μm to 80 μm of the effective aperture.
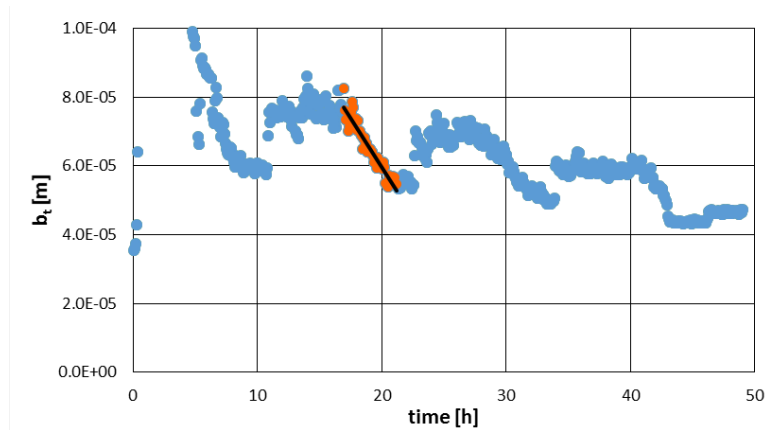

Fig. 12 Change in the aperture of the flow path with time. (Ca: 7.5 mM)

The estimated deposition rates and the outflow rate of CSH were summarized in Table. 2. As shown in Table 2, the estimated deposition rates of CSH were large enough to clog locally in the flow path, and the outflow rates were much smaller than the deposition rate. For example, assuming that CSH homogeneously deposits on the surface of the flow-path (300 mm^2 of the cross section in Fig. 3), the decrease rates of the aperture based on the deposition-volume rate in Table 2 are estimated as about 10 μm/h.

Besides, although the apparent deposition rate-constant of CSH for the lower concentration of Ca became obviously larger than those for the higher one, the apparent deposition rates were almost same in the range of 0.3 mM to 7.5 mM in injected concentration of Ca ions, and the outflow rates for the higher concentration of Ca were a little larger than those for the lower one. These suggest that even if under the condition of lower concentration of Ca, Ca ions were excess for forming

CSH on the flow-paths, while CSH formed under the condition of the higher concentration of Ca will be relatively easy to move. Such a behavior seems harmonic to also the relation of Ca concentration to the eluted Si concentration in a pseud steady state showing 1.0×10^{-10} to 2.0×10^{-10} m^2 in permeability, as shown in Fig. 9.

Table. 2 Deposition rates and outflow rates of CSH, and other parameters used for the calculation.

$Ca(OH)_2$ [mM]	slope [1/h]	Deposition rates constant [m/h]	Deposition rates [mol/h]	Deposition-volume velocity [mm^3/h]	CSH outflow rates [mol/h]	Outflow-volume velocity [mm^3/h]
0.3	−6.20E−06	1.09E−01	1.01E−05	3.14	3.05E−08	9.51E−03
2.5	−9.76E−06	2.11E−02	1.59E−05	4.95	2.99E−08	9.34E−03
6.4	−3.98E−06	3.34E−03	6.47E−06	2.02	3.42E−08	1.07E−02
7.5	−5.68E−06	4.10E−03	9.24E−06	2.88	3.83E−08	1.20E−02
	CSH density [mol/mm^3]		3.20E−06	flow-path volume [mm^3]		24

This study showed through micro-flow cell experiments that the local and heterogeneous formation of CSH under the highly alkaline Ca-rich condition significantly contributed to the clogging effect of micro flow-paths. These results suggest that CSH deposition and clogging is occurred in groundwater flow path of natural barriers around repository under a high pH condition. Furthermore, the influence of Ca concentration on clogging was not confirmed. This suggested that the amount of CSH was controlled by Si elution under a high pH and Ca condition.

CONCLUSIONS

In this study, the influence of the Ca concentration on the clogging effect with the formation of CSH in the micro flow-paths was examined. As a result, the permeability in the flow path decreased with the deposition of CSH under all conditions of Ca concentration. In addition, once the permeability decreased, the lower permeability was kept with increasing and decreasing repeatedly. From the estimation of the deposition and outflow rate of CSH, this periodical change in the permeability will be due to competing the deposition of CSH in the flow path and the outflow of CSH particles. Under the highly alkaline Ca-rich condition in this study, the amount of CSH formed in the flow path was probably kept constant without the dependencies of Ca concentration due to the restriction of the amount of Si dissolved from granite. Most CSH would contribute the clogging effect in the flow-paths under the experimental conditions of this study because the deposition rates of CSH were much larger than the outflow rates. These results in this study suggest that the continuous feed of Ca ions from the geological repository with large amount of cements will retard the migration of radionuclides by clogging flow-paths with the formation of CSH under a high pH condition.

REFERENCES

1. A. ATKINSON, "The Time Dependence of pH within a Repository for Radioactive Waste Disposal," AERE R 11777, UKAEA (1985).

2. 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).

3. D. Kurata, Y. Niibori, T. Chida and H. Mimura: Estimation of permeability change due to contact with highly alkaline Ca-rich solution by using micro flow-cell of granite chip − 14094, Proc. of WM2014, Paper-No.14094 (2014).

4. Japan Nuclear Cycle Development Organization Institute and the Federation of Electric Power Companies of Japan: Second progress Report on Research and Development for TRU Waste Disposal in Japan, JNC-TY1400-2005-013, Chapter VI (2005).

5. T. Chida, D. Kurata, Y. Niibori, H. Mimura: Influence of Temperature on Permeability Changes of Flow-paths Altered by Highly Alkaline Ca-rich Groundwater, Proc. of WM2015, Paper No. 15192 (2015).

6. K. Okumura, A. Sasahira, K. Noshita, T. Yoshida, K. Kato, S. Nagasaki, T. Ohe: A fast and sensitive method for evaluating nuclides migration characteristics in rock medium by using micro-channel reactor concept, Physics and Chemistry of the Earth, **32**, 463-468 (2007).

7. K. Okumura, A. Sasahira, K. Noshita, T. Ohe: A method for determining both diffusion and sorption coefficients of rock medium within a few days by adopting a micro-reactor technique, Applied Geochemistry, **23**, 2130-2136 (2008).

8. JNC (Japan Nuclear Cycle development institute): H12 Project to Establish the Scientific and Technical Basis for HLW Disposal in Japan, JNC TN1400 99-023 (1999).

9. A.P. Oron, and B. Berkowitz: Flow in rock fractures, The local cubic law assumption reexamined. Water Resources Research, **34**(11), 2811-2825 (1998).