Estimation of Permeability Changes due to Contact with Highly Alkaline Ca-rich Solution

by Micro Flow-Cell of Granite Chip – 14094

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ABSTRACT

Groundwater around a disposal site is highly alkalized by long term contact with cementitious materials used for constructing the repository. In such a situation, a main concern is the chemical/physical influences of highly alkaline groundwater (plume) on the multi-barrier systems. That is, highly alkaline plume might dissolve some silica or silicate minerals, and form calcium-silicate-hydrate (CSH) with relatively low Ca/Si molar ratio as a secondary mineral. Besides, since such an alkaline plume includes Na, K and Ca ions (which control the pH value in the range from 12.5 to 13.5), the permeability of the flow-paths would complicatedly change in the region downstream from the repository. Using a micro flow-cell consisting of silicon plate (including a slit) and granite-chip, this study examined the change of the permeability of flow-paths contacted with high alkaline solution. Furthermore, its deposition rate of CSH was also estimated. Besides, the distribution of CSH deposition was observed by the digital microscope and the two-dimensional element mapping of EDX (Energy-dispersive X-ray spectroscopy).

The experimental results showed that the flow rate affected the overall permeability of the micro flow cell and the apparent rate constant of the deposition reaction of CSH. Besides, the deposition of CSH was not uniformly distributed on the surface. The EDX mapping suggested that quartz might play a role for supplying the silicic acid under a highly alkaline condition. Furthermore, the deposition rate constant was in the range from 2.08×10^{-4} m/s to 2.75×10^{-3} m/s. Such partial clogging of Ca-deposition on the silicate minerals would change flow-channels, forming a natural barrier around the repository, when cementitious materials maintain pH higher than 10 for 10^4 years around the repository.

INTRODUCTION

High level radioactive wastes containing the radionuclides of long half-lives [1] must be isolated from accessible environments for a long period of time. The geological disposal is a passive way to ensure long-term safety by using a multiple barrier system [2]. Since a Japanese disposal system is predicted to be under a condition saturated with groundwater, a huge amount of cement materials are required for the construction as in other countries. Therefore, we should consider various influences of the cement materials on the multiple barrier system. In general, cementitious materials elute Na and K ions in the early stage, altering groundwater up to around 13 in pH [3]. After that, Ca ions control the pH of groundwater (shifting pH to 12.5). Since the solubility of silicic acid becomes extremely large in the range of pH exceeding 9.5, such a highly alkalized groundwater might dissolve some silicates or form calcium silicate hydrate (CSH) on the flow-paths included in the natural barrier. In this study, the changes of the permeability due to the contact of the granite surface with highly alkaline solution were examined by using a micro flow-cell consisting of silicon plate (including a slit) and granite-chip.

EXPERIMENTAL

Figure 1 shows an illustration of the experimental apparatus using the micro flow cell (its detail is mentioned below in Figure 2). As a solution injected into the micro flow cell, this study used a $Ca(OH)_2$ solution (8.5 mM) adjusted to pH 12.2 to 12.5 with NaOH solution. The value of 8.5 mM almost corresponds to the Ca concentration of pore water of cement [4]. This study followed the basic experimental procedures already reported by the authors [5]. The solution was injected continuously into the micro flow cell by a syringe. The permeability of the flow path was monitored by a pressure gauge. In order to avoid the contact of the solution with carbon dioxide, purified nitrogen was continuously passed through the fraction collector. The concentrations of Ca and Si ions in the solution eluted from the flow-cell were measured by using ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry instrument), and the pH value was also monitored. Besides, the distribution of CSH deposition was observed by the digital microscope. Furthermore, by using the two-dimensional element mapping of EDX (Energy-dispersive X-ray spectroscopy), the distribution of calcium and the other elements on the granite surface was examined.

Figure 2 shows the inner structure of micro flow chip. The flow-path was prepared by nipping the Teflon sheet of 80 μm in thickness between the granite chip and the basement of Teflon. The Teflon sheet has a slit with a given width, w (2 mm or 5 mm), and the length of the slit, x_1, along the flow direction was set to 60 mm. The granite chip was roughly ground with #2000 (ϕ 7.9 μm, SiC grinding powder). The granite sample consisted of quartz 30%, microcline 22.5%, albite/anorthite 22.5%, biotite 5% and impurities 10% in weight percent. **Table I** summaries the experimental conditions in this study. Here, the injection flow rate was set to a given rate in the range of 0.2 ml/h to 2.0 ml/h by a pump used for chromatograph.
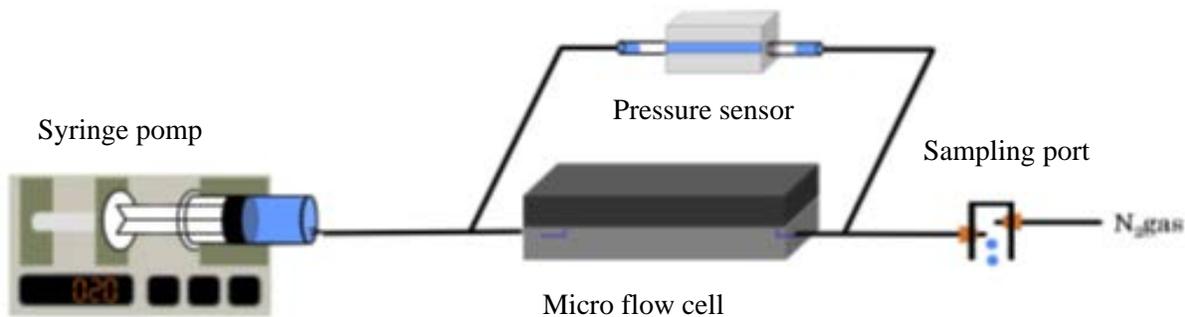
Fig.1. The schematic view of an experimental apparatus
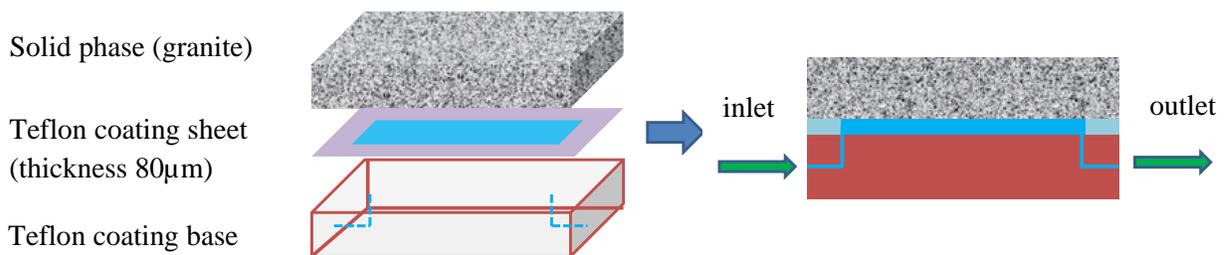
Fig.2. The inner structure of a micro flow cell

Table I. Flow test conditions

Sample Name	A	B	C	D	E
1) Flow Rate (ml/h)	2	1	0.5	0.2	0.2
2) Ca ions concentration (mmol/l)	8.5	8.5	8.5	8.5	0

RESULT AND DISCUSSION

Measurement of Permeability

Based on Darcy's law, the overall permeability, k (m^2), of the micro flow cell is evaluated by using

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

where v is Darcy's fluid flow velocity (m/s) , μ is fluid viscosity (Pa·s), p is pressure (Pa), x_1 is the length of flow cell along flow direction (m), and the subscripts, in and out, mean the inlet ant outlet of micro flow cell, respectively. Besides, the volume flow rate, Q (m^3/s) yields

$$Q = wbv, \tag{2}$$

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

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

Furthermore, using the estimated b and $k = b^2/12$, we can obtain the overall permeability k.

Influence of the Flow Rate on Overall Permeability

Figures 3 and **4** shows the permeability changes with time. Here, the constant flow rates were set to 2 ml/h (Sample name: A) and 1 ml/h (Sample name: B), respectively. The overall permeability gradually decreased due to the deposition including Ca, while some oscillations were observed in the permeability. Besides, it was confirmed that the detached precipitation flowed out of the micro flow-cell. Furthermore, such a precipitation flowing out of the flow cell and the deposits from the surface of granite chips were dissolved in the distilled water of pH=5.6 and the chemical components in the water showed that the precipitation and the deposits were calcium-silicate-hydrate (CSH) [5]. When the flow rate is fixed at a constant one even if the flow paths narrow due to the deposition of CSH, the pressure gradient increases in the flow cell. Therefore, some parts of CSH occasionally flowed out of the micro flow cell, indicating the oscillations in permeability.

Figures 5 and **6** show the permeability with time, where the constant flow rates were set to 0.5 ml/h (Sample name: C) and 0.2 ml/h (Sample name: C). The initial permeabilities of C and D slightly increased compared to those of A and B. Besides, a lower flow rate, that is, a smaller pressure gradient through the whole of the flow cell, suggests that more amount of CSH was retained in the experiment of C and D. This might lead more violent change of the overall permeability as shown in Figures 5 and 6.

Figure 7 shows the permeability change with time in the experiment using sodium hydroxide solution (pH 13.5). When the Ca-free highly alkali solution was continuously injected on the granite chip, the permeability gradually increased with time. As mentioned above, since the solubility of silicic acid becomes large as pH exceeds 9.5, such a NaOH solution dissolves the surface of granite chip consisting of silicates, increasing the overall permeability in the micro flow cell. In other words, Ca ions in alkali solution lead the decrement (or oscillation) of the permeability as shown in Figs. 3 to 6.

Besides, the concentrations of Ca and Si ions, and pH were monitored at the outlet of micro flow cell. **Table II** indicates the measurement results. While the concentration Ca ions did not so much decrease compared to the injection concentration, the concentration of Si ions was not detected. Besides, in each experiment, the value of pH at the outlet was almost similar to that of the injection solution. These mean that the feed amounts of Ca ions were enough to form CSH, while the soluble silicic acid was perfectly consumed in the experimental conditions of this study.

Table II. Change of concentration and pH in each experience

2 ml/h				1 ml/h			
	Concentration [mM]				Concentration [mM]		
Sample No	Ca	Si	pH	Sample No	Ca	Si	pH
1	7.89	0	12.02	1	8.65	0	12.35
2	7.67	0	11.98	2	7.36	0	12.28
3	8.00	0	12.02	3	8.04	0	12.33
0.5 ml/h				0.2 ml/h			
	Concentration [mM]				Concentration [mM]		
Sample No	Ca	Si	pH	Sample No	Ca	Si	pH
1	8.43	0	12.41	1	8.39	0	12.35
2	7.96	0	12.01	2	8.12	0	12.06
3	8.07	0	12.13	3	7.78	0	12.28
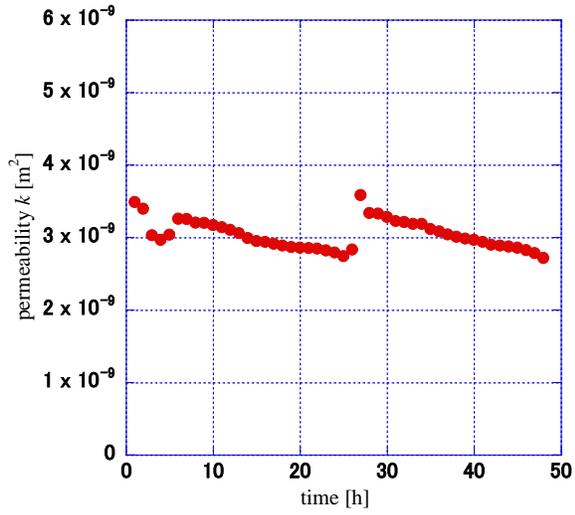
Fig. 3. Change of permeability (2 ml/h)
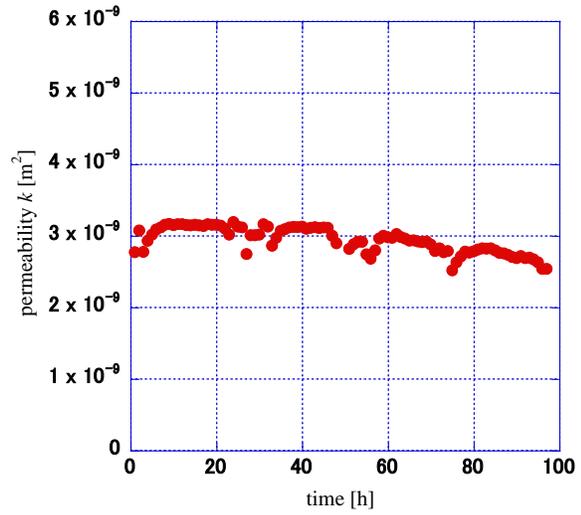
Fig. 4. Change of permeability (1 ml/h)
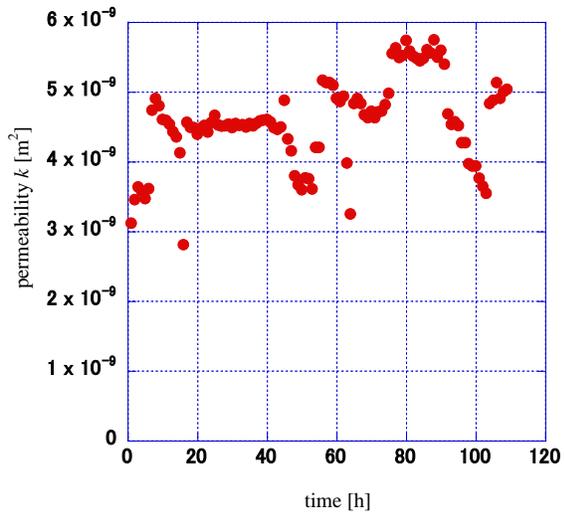
Fig. 5. Change of permeability (0.5 ml/h)
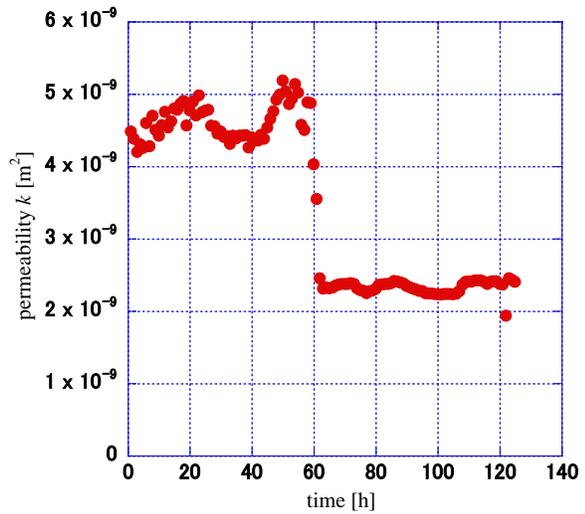
Fig. 6. Change of permeability (0.2 ml/h)
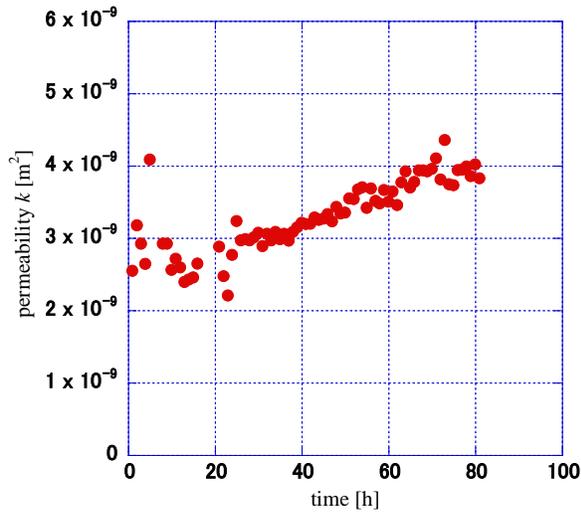
Fig. 7. Change of permeability (0.2 ml/h)

Surface Observations of Granite Chip

Figure 8 shows the surface of granite sample in the state before injecting the alkaline solution. The surface was observed by a digital microscope and SEM. As shown in Figure 8, the surface was relatively flat, even if the surface was roughly ground. In the same way, **Figure 9** shows the surface observed after the experiment. The deposition of CSH was clearly observed in comparison with Figure 8. Furthermore, Figure 9 shows that the deposition was not uniformly distributed. That is, the CSH deposited along local flow channels. Therefore, these results suggest that such local changes on the surface affected the overall permeability of micro flow cell. Besides, **Figures 10 and 11** show the distribution of Ca on the surface before and after the experiment, respectively. (The locations were not perfectly same.) Since the alkali feldspar such as anorthite includes Ca element, Ca was observed on the surface even if in the state before the experiment. Figure 11 shows more Ca element due to the deposition. Besides, in Figure 11, the area of relatively few Ca element was observed. This area corresponded to the surface of quartz. That is, quartz might play a role for supplying the silicic acid under the high alkaline condition.
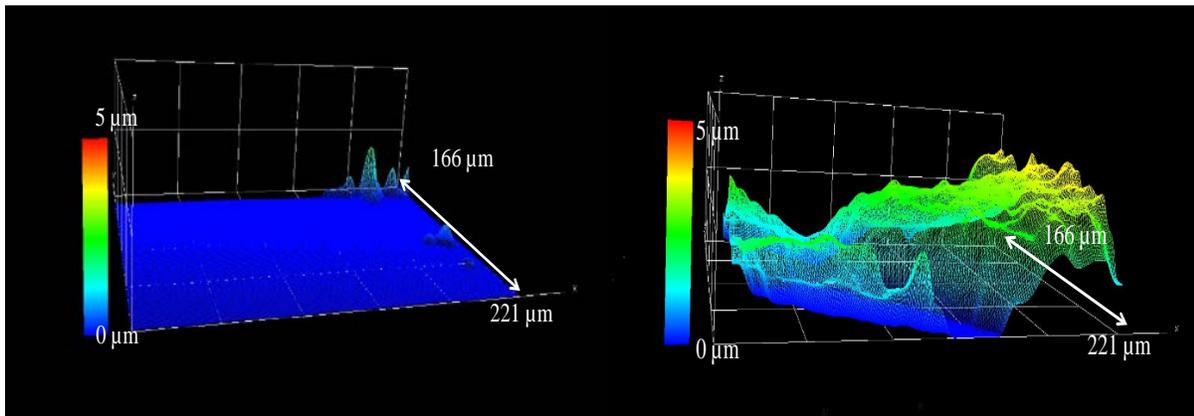
Fig. 8. The surface of granite chip in the state before an experiment (the case of D)

Fig. 9. The surface of granite chip observed after an experiment (the case of D)

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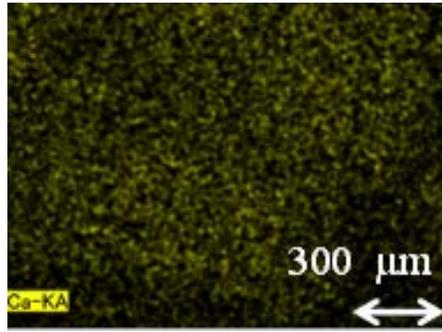
Fig. 10. Ca distribution on granite surface before the injection of Ca(OH)$_2$ solution in the experiment D
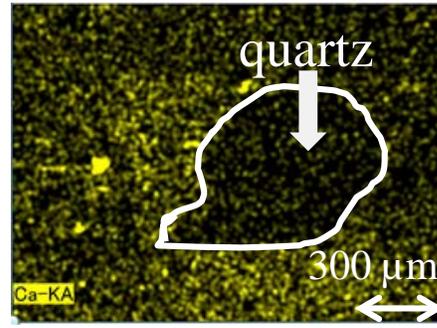
Fig. 11. Ca distribution on granite surface after the injection of Ca(OH)$_2$ solution in the experiment D

Evaluation of Deposition Rate

From Table II, it was confirmed that Ca ion was enough to form CSH on the surface. This means that the concentration of Ca ions was nearly constant in the experiments of this study. Furthermore, the pH was highly maintained through the micro flow cell. Therefore, this study evaluated the apparent deposition rate constant by assuming the one-order reaction and a constant Ca concentration. The rate constant k_R (m/s) is described by

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

where ρ_M is the density of CSH (mol/m^3), b_0 is initial aperture of flow-path (m), and b is aperture of flow path at time t (s). Furthermore, when c is approximately equal to c_{in} (the injection concentration of Ca ions) as show in Table II, the apparent rate constant can be evaluated by using equation (4).

Figure 12 shows the average values of apparent deposition rate constants estimated from the time ranges where the permeability decreases. When ρ_M is 2.0×10^3 kg/m^3, the apparent deposition rate constants were in the range of from 2.08×10^{-4} m/s to 2.75×10^{-3} m/s, depending on the flow rate. Generally, if the reaction rate is controlled by mass transfer, the apparent rate constant increases with increment in flow rate. However, the estimated rate constants showed the opposite tendency, as shown in Figure 12. When the flow rate is relatively larger, the precipitation of CSH can more easily flow out of the flow-cell system. This might decrease the apparent rate constant. Furthermore, we can consider the one-dimensional, advection-dispersion model including the deposition rate [6]. The model has a key non-dimensional parameter, i.e., Damköhler number, $D_a = x_1 a k / u_0$, where x_1 is the characteristic length (length of flow-path), a is the specific surface area (=2/b) (1/m) and u_0 is the fluid flow velocity of groundwater (m/s). Assuming u_0=1 to 50 (m/year), x_1=1.0 m, a=2.0×10^3 to 2.0×10^4 (corresponding to the initial aperture of the flow path =0.1 mm to 1.0 mm) [7] and k=2.08×10^{-4} m/s to 2.75×10^{-3} m/s, D_a is estimated to be larger than 10^5. Such a large value of D_a suggests that the deposition of CSH remarkably changes the flow paths around the repository of radioactive wastes.
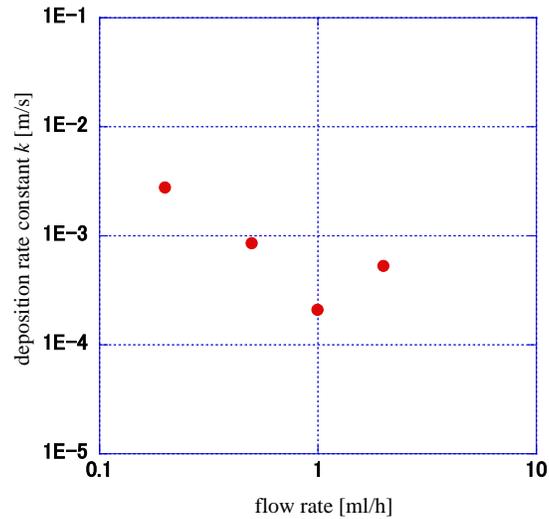
Fig. 12. Deposition rate constant of each experiment

CONCLUSIONS

Using a micro flow-cell and granite-chip, this study examined the change of the permeability of flow-paths contacted with high alkaline solution. Furthermore, its deposition rate of CSH was also estimated. The results showed that the deposition was not uniformly distributed on the surface. Besides, the flow rate affected the overall permeability of the micro flow cell and the apparent rate constant of the deposition reaction. The rate constants were in the range of from to in the range from 2.08×10^{-4} m/s to 2.75×10^{-3} m/s. Furthermore, EDX results suggested that quartz play a role for supplying the silicic acid under a highly alkaline condition.

Since CSH is stable in the range of pH larger than 10, such partial clogging of Ca-deposition on the silicate minerals would change flow-channels, forming a natural barrier around the repository, when cementitious materials maintain pH higher than 10 for 10^4 years around the repository. As a more reliable experimental condition, we can consider also a constant pressure gradient instead of a constant flow rate. Such an experiment might limit the outflow of the deposits from the flow-cell system. This means an easier formation process of the deposits in comparison with the experiments of this study done under the constant flow-rate condition.

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