

**Alteration Behaviors of Granite Minerals Forming Calcium Silicate Hydrate
under Ca-Rich Highly Alkaline Conditions – 16160**

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ABSTRACT

Cementitious materials used for geological disposal systems leach large amounts of alkaline ions (Ca^{2+} , Na^+ , K^+) into groundwater, and alter the pH of groundwater by up to 13. The altered groundwater contacts the host rock and forms Calcium-Silicate-Hydrate (CSH) through the interaction of Ca ions and the silicate species, which in turn clogs the flow paths of the host rock. This clogging effect in the flow paths is expected to retard the migration of radionuclides. A previous study reported the heterogeneous formation of CSH on the surface of granite under Ca-rich and highly alkaline conditions. To clarify the formation process of CSH, this study examined the CSH formation with the dissolution of some minerals contained in the granite under Ca-rich and highly alkaline conditions. In the experiments, the granite block and the crushed minerals contained in the granite were immersed in a 6.4-8.5 mM $\text{Ca}(\text{OH})_2$ solution adjusted pH to 12.5 by adding NaOH solution. As a result, biotite and anorthite supplied more Si to the formation of CSH than other minerals. Furthermore, most of the formed CSH precipitated on the solid surface although a little CSH remained in liquid phase as supernatant. These results suggest that under Ca-rich highly alkaline conditions the CSH formed as a secondary mineral will retard the migration of radionuclides released from the repository because of the clogging effect of the flow path.

INTRODUCTION

Large amounts of cementitious materials are required for the construction of geological disposal systems for high level radioactive waste. After the closure, cementitious components, such as calcium (Ca), sodium (Na) and potassium (K), leach from these cementitious materials, and alter groundwater to a highly alkaline condition (about pH 13) around the repository. Such conditions will affect the migration of radionuclides because the chemical and physical properties of the host rock around the repository are dramatically changed by the dissolution of silicate minerals and the formation of secondary minerals [1]. Of them, calcium-silicate-hydrate (CSH), formed by the interaction of Ca ions and silicate species under highly alkaline conditions, might play one of the most important roles in retarding the migration of radionuclides. The formation of CSH around the repository not only alters the solid surface for the sorption of radionuclides, but also clogs the flow paths of the host rock. This clogging effect is expected to increase the retardation effect with the decrease in permeability. We previously showed the heterogeneous

formation of CSH on the surface of granite and the clogging of the micro flow-path under highly alkaline and Ca-rich conditions based on related flow-experiment results [2]. This heterogeneity of CSH formation means that the supply (or dissolution) of silicate species on the granite surface is not homogeneous because granite consists of several minerals, including quartz, and biotite, and the dissolution behaviors of these minerals under highly alkaline conditions are not uniform. Therefore, to obtain fundamental knowledge about the formation process of CSH in the flow paths of host rock, this study focused on the dissolution behaviors of several minerals contained in granite under highly alkaline and Ca-rich conditions, and on the formation of CSH with such alterations.

EXPERIMENTAL

In the experiments, granite and component minerals (quartz, biotite, anorthite, orthoclase and albite) were prepared as powder samples (particle size: 75 - 149 μm). To observe the alteration of a solid surface, block samples of granite were also prepared (80×25×10 mm). Besides, two kinds of immersion solutions were examined: 6.4-8.5 mM $\text{Ca}(\text{OH})_2$ solution simulating fresh groundwater containing cement compositions, and 6.4-8.5 mM $\text{Ca}(\text{OH})_2$ in 0.45-0.6 M NaCl simulating the saline groundwater. The pH of these solutions was adjusted to 12.5 by adding 0.1 M NaOH. The liquid-to-solid weight ratio (L/S ratio) was set to 50 for powder samples (0.24g). The block samples were immersed in 75 mL of solution. Using sample tubes with caps, the solid samples were immersed in each solution for 7-63 days with shaking. The procedure of submerging the solid samples into the solution was carried out in a glove bag saturated with nitrogen gas to avoid the formation of calcium carbonate. After separating solid and liquid phases with the filtration (filter size: 0.45 μm), the surface of the block samples was observed by Scanning Electron Microscope / Energy Dispersive Spectrometry (SEM/EDS, Hitachi High-Tech, Miniscope TM3030) and Digital Micro Scope (DMS, Keyence Corporation, VHX-5000). For the solution samples, the average particle size of CSH gel with a diameter less than a given filter size and its zeta potential of supernatants were measured by dynamic light scattering measurements (Otsuka Electronics Co., Ltd., ELSZ-2PLUS), and the concentrations of Ca and Si were monitored by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Seiko Instruments Inc., SPS7800).

RESULTS AND DISCUSSION

Figures 1 and 2 show the change in the concentrations of Si and Ca for the immersion experiments. As shown in Fig. 1(a) and Fig. 2(a), the concentrations of Si leached from biotite and anorthite exceeded those from other minerals. This means that biotite and anorthite supply more Si to the liquid phase under these conditions. Furthermore, even though the concentration of Si from quartz was less than half of those supplied from biotite and anorthite, quartz is also one of the main suppliers of Si because of its high content ratio (40%) in granite [3]. Therefore, these three minerals in granite strongly contribute to the formation of CSH. In Fig.

1(d) and Fig. 2(d), the concentration of Ca for biotite and anorthite decreased more than those for other minerals. This suggests that more Ca is consumed for the formation of CSH under the condition of supplying more Si. Besides, the significant decrease in the concentration of Si at 63 days in Fig. 1(a) will be due to the precipitation of CSH with the progress of CSH formation. Additionally, the amounts of Si leached from all minerals under the condition of saline groundwater exceeded those of fresh groundwater. According to chemical equilibrium theory, this occurs because the high ion strength of saline groundwater causes an increase in the solubility of Si species such as silicate minerals and CSH.

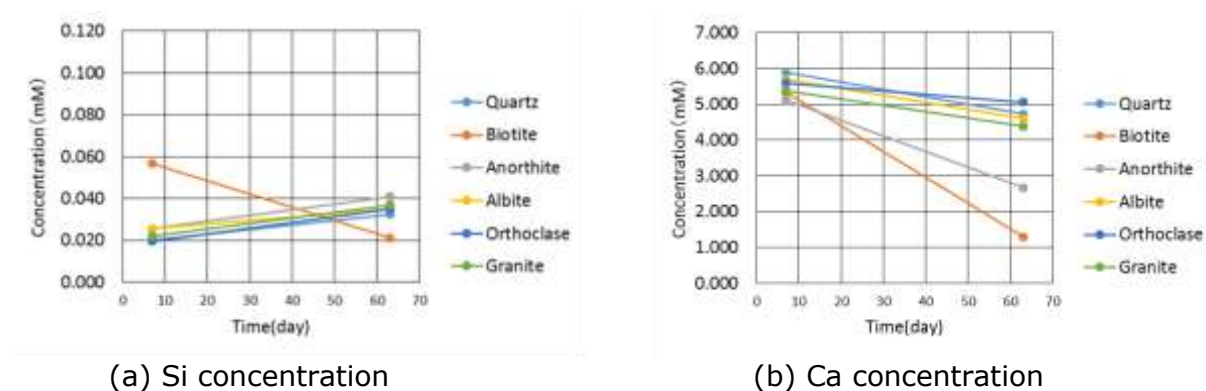


Fig. 1. Changes in the concentrations of Si and Ca for experiments (Fresh groundwater)

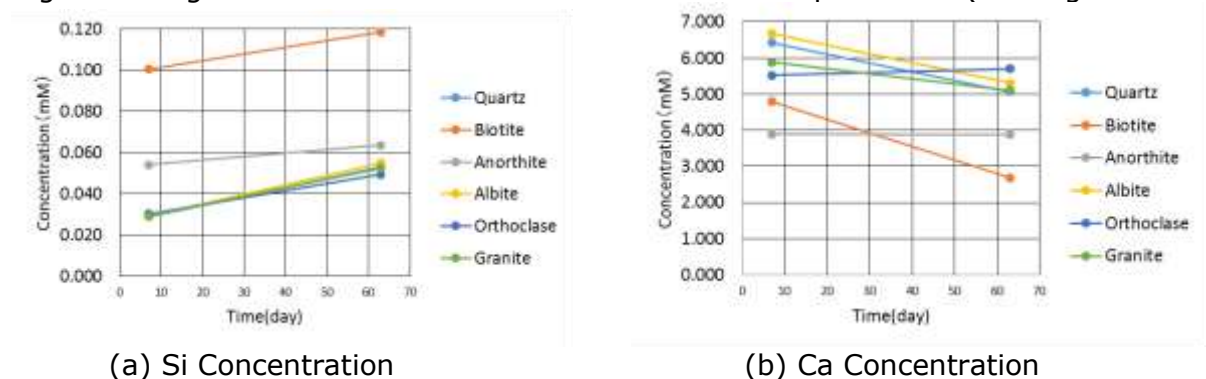


Fig. 2. Changes in the concentrations of Si and Ca for experiments (Saline groundwater)

Seven days later, CSH particles under the condition of fresh groundwater could not be detected. On the other hand, CSH particles under the condition of saline groundwater were in the range of diameter from 200 to 2000 nm, whose size exceeded the filter size due to the crosslinking with the addition of electrolytes. Besides, at 63 days, CSH particles were not detected under the condition of both fresh and saline groundwater because the particle size became larger than the detection limit (over 2000 nm) with the polymerization in liquid phase after the separation. These results suggest that CSH particles become larger and precipitate on the solid surface with the progress of the CSH formation, though some CSH is in liquid phase. Besides, the zeta potential for most samples showed a negative charge. This means that the Ca/Si molar ratio of the formed CSH is relatively low ($\text{Ca/Si} < 1.0$) in spite of the Ca-rich condition [4, 5]. Previous studies have reported that the CSH of lower Ca/Si ratio shows a higher sorption effect for the radionuclides of metal ions (cation) such as Cs^+ , Ba^{2+} and Eu^{3+} [6, 7]. Therefore, the precipitation of such CSH on the solid phase may increase the retardation effect on the migration of radionuclides.

Figures 3 and 4 show the distribution of elements on the surface of the block sample by SEM/EDS. As shown in Fig. 3 and Fig. 4, the distribution of Ca slightly increased, and that of other elements did not remarkably change in this experiment. Here, the distribution of Ca in Fig. 3 is caused by anorthite contained in granite [8].

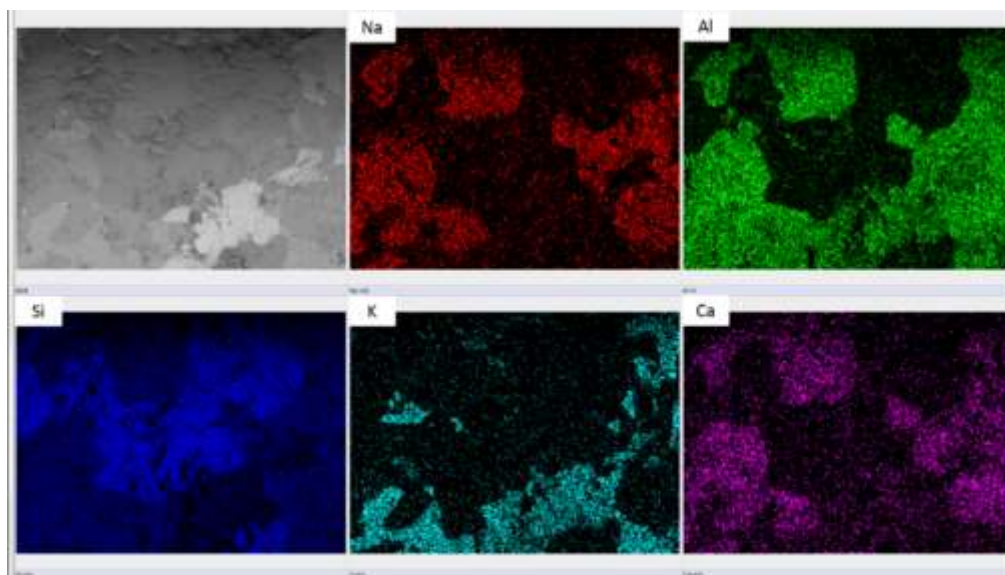


Fig. 3. Distribution of elements on the surface of granite before the experiment by SEM/EDX.

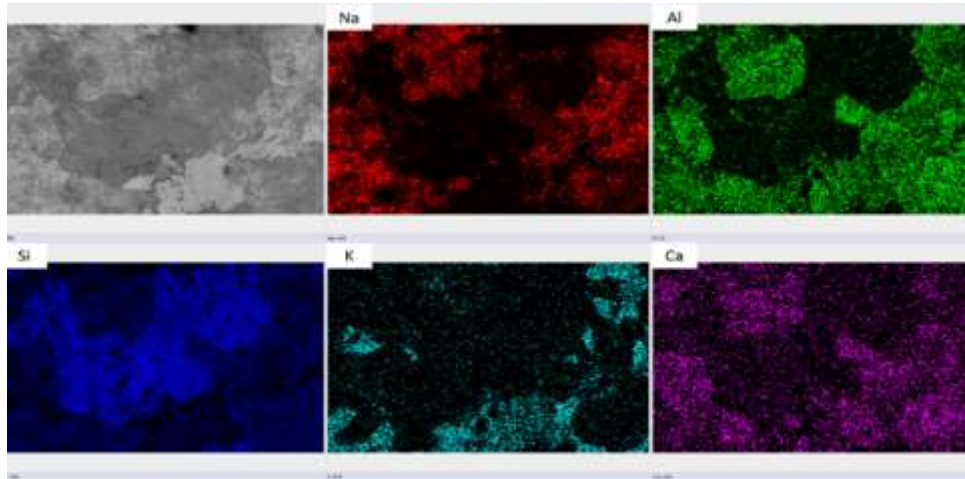


Fig. 4. Distribution of elements on the surface of granite after the experiment by SEM/EDX. (The block sample immersed in saline groundwater for 41 days.)

Figure 5 shows the alteration of the granite surface before and after the experiments by DMS. Figure 5(a) and Fig. 5(b) show the same area on the surface of the block sample. In Fig. 5(b), the areas of biotite (black areas) on the granite surface increased in comparison with Fig. 5(a) (For example, see Points A and A' indicated by white circles). Such alteration is due to the dissolution of minerals covering the biotite. Figure 6 shows the height distribution of the block sample before and after the experiments by DMS, in which the analysis area was the same area as that in Fig. 5. The height differences in Fig. 6(b) became smaller than those in Fig. 6(a) as can be seen when comparing Points B-C in Fig. 6(a) with B'-C' in Fig. 6(b). In addition, Point D' in Fig. 6(b) locally became much higher. Considering the decrease in Ca concentration in Fig. 2(b) and the distribution of Ca on the whole granite surface shown in Fig. 4, the precipitation of CSH will contribute to such change in the physical property of the granite surface, even if the presence of CSH on the granite surface cannot be clearly observed, as shown in Fig. 5.

These results indicate that under highly alkaline and Ca-rich conditions, CSH forms not on the granite surface but in liquid phase. Then CSH enlarges in size, precipitating on the solid surface. That is, around the repository, the CSH does not always deposit on the surface of flow-paths, but migrates as supernatant in the flow-paths such as fractures of granite, clogging the flow-paths due to its surface unevenness. Since groundwater detours to avoid the clogged flow-paths, a Ca-rich highly alkaline condition, as a result, would retard the migration rate of radionuclides released from the repository.

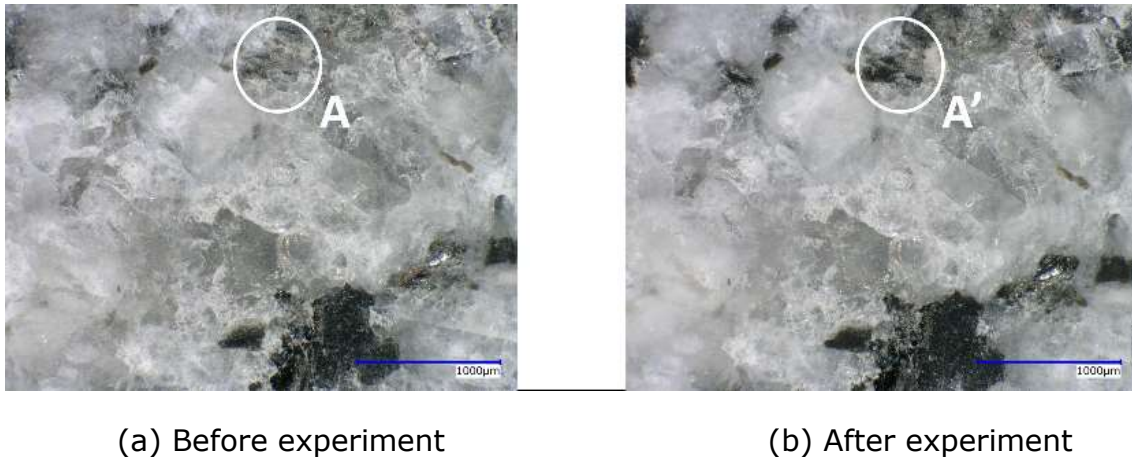


Fig. 5. DMS images
(Block sample immersed in saline groundwater for 41 days)

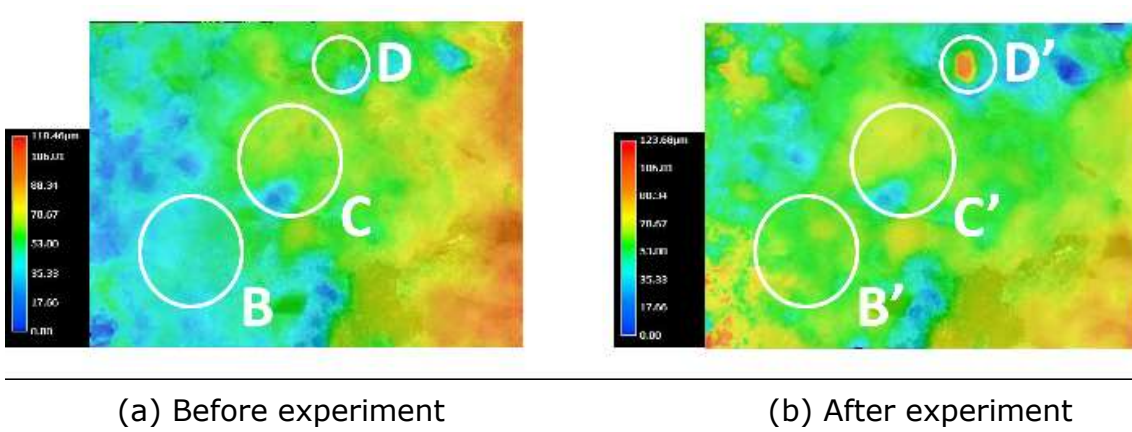


Fig. 6. Height distribution of the granite surface
(Block sample immersed in saline groundwater for 41 days)

CONCLUSIONS

This study investigated the alteration of granite forming CSH under highly alkaline and Ca-rich conditions. The results of the immersion experiments indicated that the minerals biotite, anorthite and quartz contained in granite supplied more Si to the formation of CSH. Observation by SEM/EDS and DMS showed that the CSH formed mostly precipitated on the local and whole surface of granite with smoothing the unevenness of the granite surface, even though some supernatant of CSH remained in liquid phase. These results indicate that the formation of CSH causes a retardation effect on radionuclide migration by clogging the flow path with the precipitates of CSH. In addition, the Ca/Si molar ratio of the CSH formed in these experiments was estimated to be relatively low ($\text{Ca/Si} < 1.0$) based on Zeta potential measurements. This means that the CSH formed under highly alkaline and Ca-rich conditions effectively sorbs cationic radionuclides. Under such conditions, CSH will spontaneously form as a secondary mineral around the repository. After closure of the geological disposal system, the CSH formed under the condition saturated with groundwater is expected to add a further retardation effect on radionuclide migration to the present multi-barrier system.

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