

**Interaction of Cesium and Barium Ions with Calcium Silicate Hydrate under
a Geological Temperature Condition – 16239**

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ABSTRACT

The interaction of calcium-silicate-hydrate (CSH gel) and cationic radionuclides such as cesium-135 significantly affects the assessment of radionuclide migration. This study examined the influence of temperature on the interaction of Cs and barium (Ba) ions with CSH gel because temperature generally affects chemical reactions such as sorption. In the sorption experiments, CSH gel was prepared by the hydration of CaO and fumed silica without a drying process, with Ca/Si molar ratios ranging from 0.4 to 1.6 and the liquid/solid weight ratio set to 20. The concentration of Cs and/or Ba ions was adjusted to 1.0 mM. The temperature conditions during the sorption experiments for 14 days were set to 298, 313 and 333 K. As a result, the sorption of Cs ions on CSH gel increased at higher temperature. Moreover, Raman spectroscopy studies showed that the silicate chain of CSH gel depolymerized with the increase in temperature. That is, the structural deformation of CSH gel at a relatively high temperature facilitates the sorption of Cs ions. On the other hand, the sorption of Ba ions on CSH gel remained high (90 %) regardless of temperature, and hardly affected the sorption of Cs ions. These findings suggest that CSH gel around the repository is expected to further retard the migration of cationic radionuclides under temperature condition up to 333 K.

INTRODUCTION

For the assessment of radioactive waste disposal systems, calcium-silicate-hydrate (CSH gel) is one of the most important factors. A large amount of CSH gel is not only contained in cementitious materials used for the construction of the repository, but also formed as a secondary mineral around the repository because the calcium (Ca) ions leaching from cementitious materials or dissolving in groundwater by nature react with silicate species, such as silicic acid, colloidal silicic acid and silicate minerals. The interaction between CSH gel and radionuclides would significantly affect the migration and immobilization of radionuclides. In particular, cesium-135 (Cs-135) highly contributes to the dose rate for the biosphere in a long-term safety assessment of the repository due to its long half-life (2.3×10^6 y) and that it dissolves in groundwater easily. It has been reported that CSH gel effectively sorbs

Cs and barium (Ba) ions at 298 K under the condition of saline water [1]. However, this previous study did not examine the influence of temperature on the sorption of Cs and Ba on CSH gel. Around the repository, temperature changes up to 333 K by the heat of radioactive waste, geothermal gradient and thermal diffusion [2]. Chemical reactions such as sorption depend on changes in temperature. To gain more fundamental knowledge of the interaction of CSH gel and cations, this study examined the influence of temperature on the sorption of Cs and Ba ions on CSH gel. Note that this study considered Cs-135 and Ba-135 (stable) produced by the beta decay (β^-) of Cs-135 as the sorption ions, and the stable isotope ions were used for the experiments. For Ba-135, this study focused on the effect of Ba-coexistence on the sorption of Cs although Ba-135 does not obviously increase the dose rate.

EXPERIMENTAL METHODS

The sorption experiments using CSH gel followed the basic procedures reported in authors' previous studies [1, 3]. In the experiments, CSH gel samples were synthesized with CaO (Wako Pure Chemical Industries Ltd.), fumed silica (AEROSIL 300 purchased from Japan AEROSIL Ltd.) and NaCl solution without a drying process. The Ca/Si molar ratios of CSH gel were set to 0.4, 0.8, 1.2 and 1.6. The concentrations of NaCl solution were set to 0, 0.006, 0.06 and 0.6 M by assuming both saline groundwater and fresh groundwater. Besides, the concentration of CsCl and/or BaCl₂ solution was adjusted to 1.0 mM in the sample solution. The total volume of the sample solution was fixed at 30 mL, and the liquid/solid weight ratio was 20 mL/g. The synthesis of each sample solution including CSH gel and Cs/Ba ions was conducted in a glove bag filled with nitrogen gas in order to prevent the carbonation of CaO powder until the sample tubes were sealed tightly. The curing period of the samples was set to 14 days with shaking at 120 strokes/min. The temperature conditions during curing were set to 298, 313 and 333 K with a thermostatic shaker.

After the curing process, each sample was centrifuged to separate the liquid and solid phase at 7500 rpm for 10 min, and the liquid phase of each sample was filtrated with a 0.20- μ m membrane filter. The concentration of Cs ions was measured by Atomic Adsorption Spectrometry (iCE 3000 series AA spectrometer, Thermo Fisher Scientific Inc.), and the concentration of Ba, Ca and Si ions was measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (SPS7800, Seiko Instruments Inc.).

As the analysis of the solid phase (CSH gel), the polymerization degree of the silicate chain in CSH gel was analyzed by laser Raman spectrophotometer (NRS-3300QSE, JASCO) used a YAG laser (532 nm) as an excitation laser. CSH gel is supposed to have a structural similarity with tobermorite, consisting of a hydrated Ca-O layer between silicate chains [4]. The polymerization degree of the SiO₄ tetrahedrons in these silicate chains is expressed as Qⁿ, where "n" is the

number of bridging oxygen atoms (siloxane bond, Si-O-Si). For example, Q^0 means that the SiO_4 tetrahedron has no siloxane bond and is a free molecule, and Q^2 means that the SiO_4 tetrahedron has two siloxane bonds and connects with the other two SiO_4 tetrahedrons. In this study, the peaks of symmetric stretching vibration of Q^1 (870 cm^{-1}) and Q^2 (1010 cm^{-1}) were analyzed by laser Raman spectrometer to estimate the polymerization degree of the silicate chain [5].

RESULTS AND DISCUSSION

Stability of CSH gel

Firstly, the influence of temperature on the Ca/Si ratios of CSH gel after curing was confirmed. Figures 1 and 2 show the concentration of Ca and Si ions in the liquid phase after curing for $NaCl=0.06\text{ M}$. As shown in Fig. 1, the concentrations of Ca ions became higher with the increase in temperature for the samples of higher Ca/Si ratio. In Fig. 2, the concentrations of Si ions did not change except for the slight increase for $Ca/Si=0.4$ with temperature. Figure 3 shows the Ca/Si ratio of CSH gel based on the concentration of Ca and Si ions in Figs. 1 and 2. The Ca/Si ratios of CSH gel were hardly influenced by the small amount of increase and decrease in the concentration of Ca and Si ions. Furthermore, the volume of water for the hydration of CSH gel did not widely change with temperature, either (Fig. 4). These findings suggest that the Ca/Si ratio of CSH gel remains constant at this range of temperature up to 333 K. Incidentally, the concentration of NaCl did not affect the Ca/Si ratio of CSH gel although the concentration of Ca and Si ions increased or decreased a little [6].

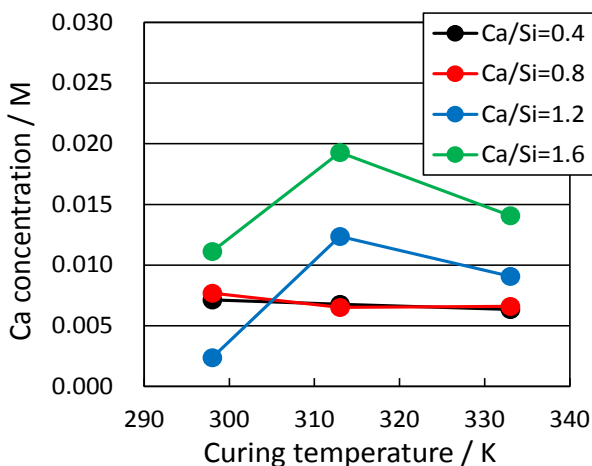


Fig. 1. Ca concentration in liquid phase after curing. ($NaCl=0.06\text{ M}$, Cs/Ba ions) (Data for 298 K were taken from Chida et al.(2015)[6])

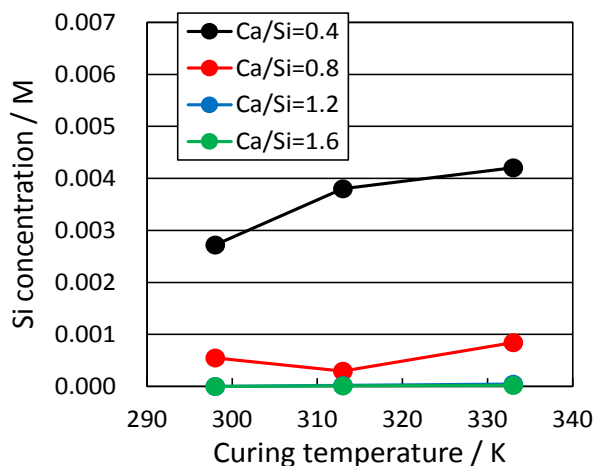


Fig. 2. Si concentration in liquid phase after curing. ($NaCl=0.06\text{ M}$, Cs/Ba ions) (Data for 298 K were taken from Chida et al.(2015)[6])

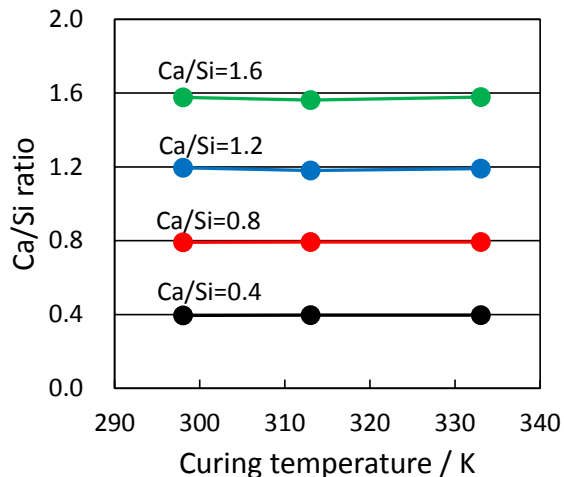


Fig. 3. Ca/Si ratios of CSH gel after curing. (NaCl=0.06 M, Cs/Ba ions)
(Data for 298 K were taken from Chida et al.(2015)[6])

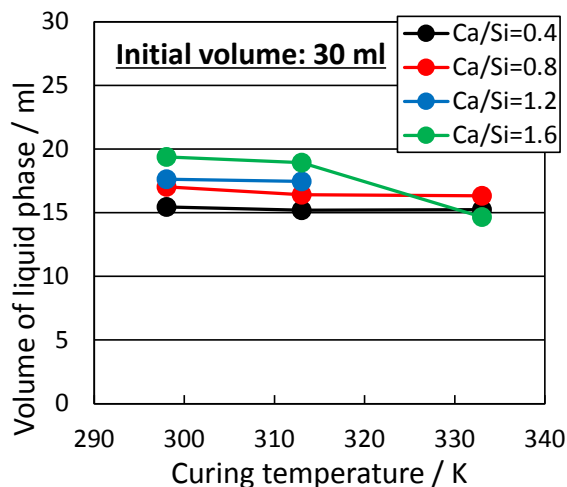


Fig. 4. Liquid phase volumes after curing. (NaCl=0.06 M, Cs/Ba ions)

Sorption of Cs and Ba ions on CSH gel

Figure 5 shows the influence of temperature on the sorption of Cs ions on CSH gel. The sorption ratio of Cs ions was estimated from the amount of Cs ions in the liquid phase after curing and the added Cs ions at the onset of sorption experiments. As shown in Fig. 5, the sorption of Cs ions on CSH gel became larger with the increase in temperature under all conditions of NaCl concentration and Ca/Si ratio. The sorption ratios of Cs on CSH gel increased from 30% to 70% in the cases of high Ca/Si ratio (>1.0) and from 70% to 90% in the cases of low Ca/Si ratio (<1.0) with changing temperature from 298 K to 333 K. On the other hand, the sorption rates of Ba ions attained about 80% and more under all conditions, and the effects of temperature were hardly confirmed (Fig. 6). Generally, the sorption of chemical species on the solid phase becomes lower with the increase in temperature. However, in these experiments, the increase in temperature facilitated the sorption of Cs ions on CSH gel and did not cause a decrease in the sorption of Ba ions. Such effects of temperature will be due to the structural alteration of CSH gel as described later. In the results of the sorption experiments for Cs/Ba ions, the sorption behavior of Cs and Ba ions was almost the same as that of Cs or Ba ions only. This suggests that Ba ions produced by β^- decay of radioactive Cs does not affect the sorption of Cs ions on CSH gel. Incidentally, the sorption of Cs and Ba ions in Figs. 5 and 6 became lower for a higher concentration of NaCl because of the inhabitation of Na ions for the sorption of Cs and Ba ions on CSH gel, as mentioned in authors' previous study [1]. Meanwhile, it is also notable to maintain a relatively high sorption ratio of Cs and Ba ions on CSH gel. This suggest that not only the electrostatic and thermodynamic equilibrium between ions and the solid

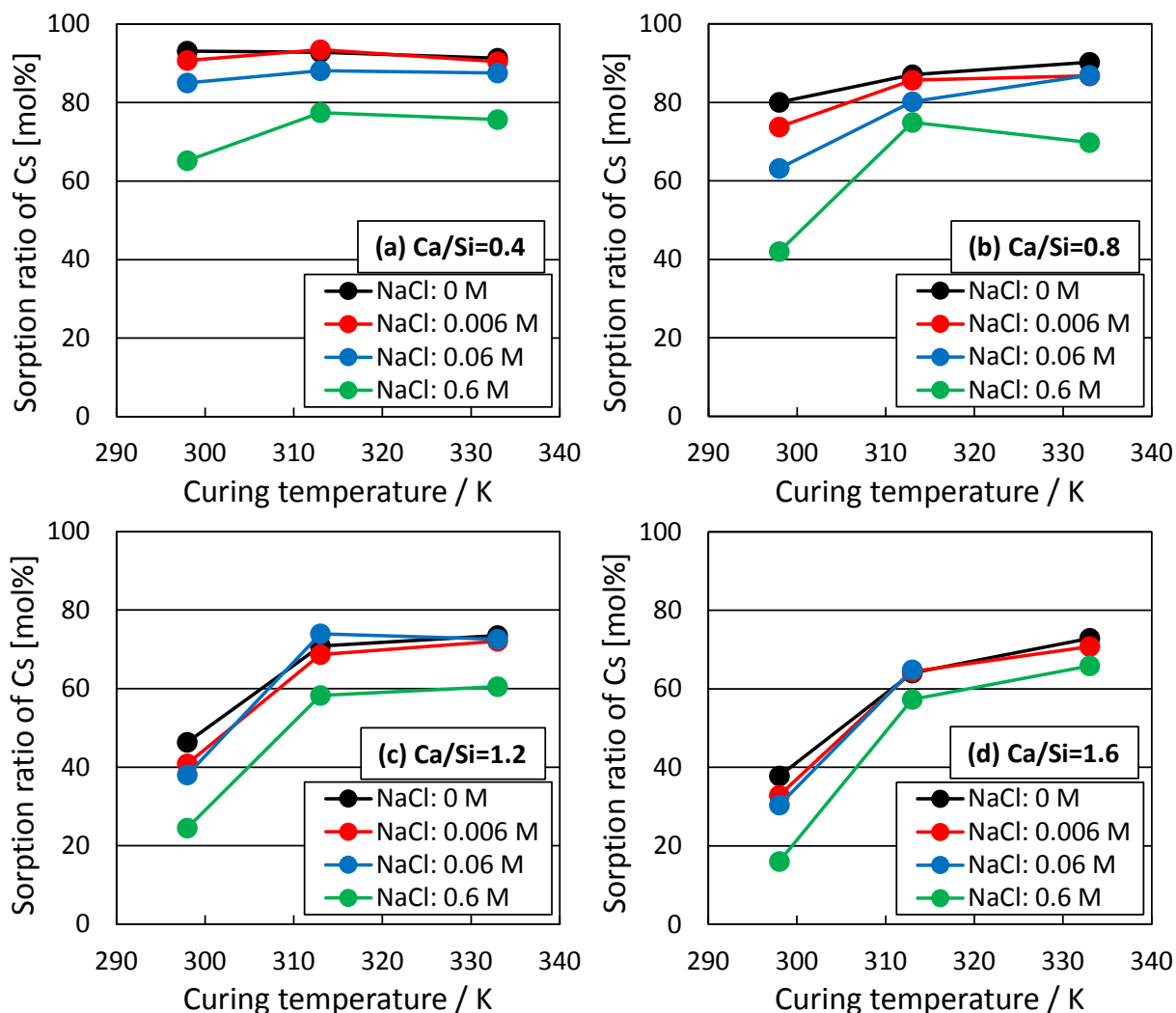


Fig. 5. Sorption of Cs ions on CSH gel. (Cs ions only) (Data for 298 K except for NaCl 0 M were taken from Saito et al.(2015)[1])

phase but also the structural alteration of CSH gel will influence the sorption of Cs and Ba ions.

Structural alteration of CSH gel

Figures 7-9 show the effect of temperature on the Q^1/Q^2 ratios estimated from the Raman spectra of CSH gel after the sorption experiments. The Q^1/Q^2 ratio is the index for the depolymerization of the silicate chain. A higher Q^1/Q^2 ratio means that the silicate chain in CSH gel depolymerizes more than the case of a lower Q^1/Q^2 ratio. The Q^1/Q^2 ratios of CSH gel with low Ca/Si ratios (0.4 and 0.8) could not be

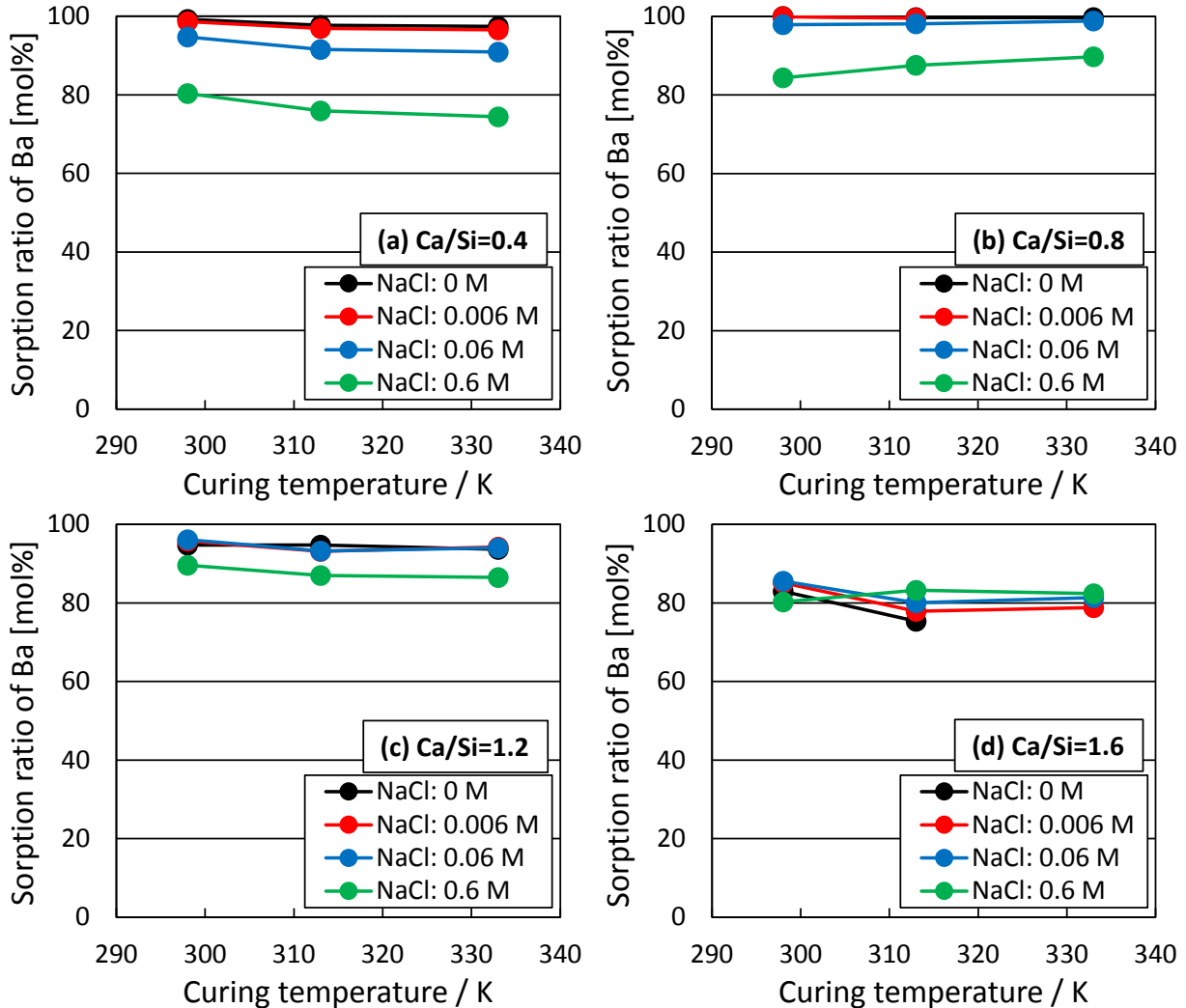


Fig. 6. Sorption of Ba ions on CSH gel. (Ba ions only) (Data for 298 K except for NaCl 0 M were taken from Saito et al.(2015)[1])

estimated because the Q^1 peak for the CSH gel was scarcely detected by Raman spectroscopy due to its high polymerization of the silicate chain. As shown in Figs. 7-9, the Q^1/Q^2 ratios became smaller at higher temperature. These results seem to show that the increase in temperature facilitates the polymerization of the silicate chain in CSH gel. However, polymeric materials generally depolymerize with increment of temperature. In addition, for a part of these data, the Q^1/Q^2 ratios increase in the temperature range up to 313 K, and decrease at 333 K. These findings suggest that the decrease in Q^1/Q^2 ratios at higher temperature is due not to the acceleration of the polymerization of the silicate chain but the depolymerization of the silicate chain corresponding to Q^1 tetrahedra, which forms

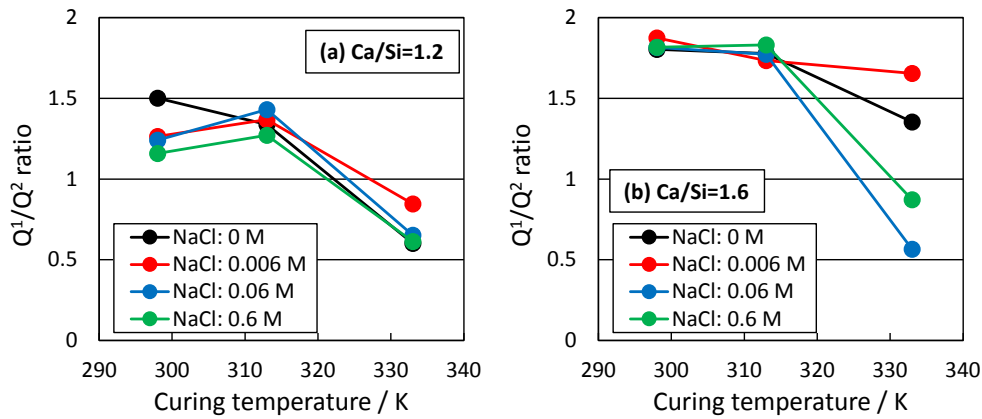


Fig. 7. Q^1/Q^2 ratio of CSH gel for the sorption of Cs ions. (Data for 298 K except for NaCl 0 M were taken from Saito et al. (2015)[1])

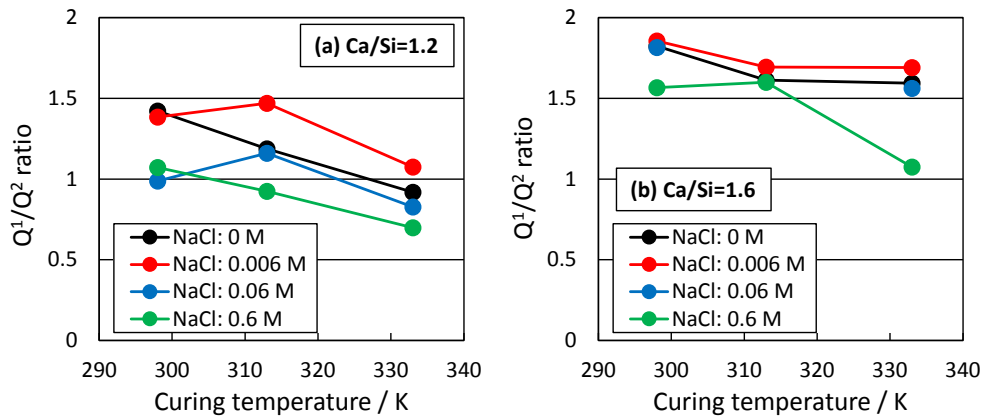


Fig. 8. Q^1/Q^2 ratio of CSH gel for the sorption of Ba ions. (Data for 298 K except for NaCl 0 M were taken from Saito et al. (2015)[1])

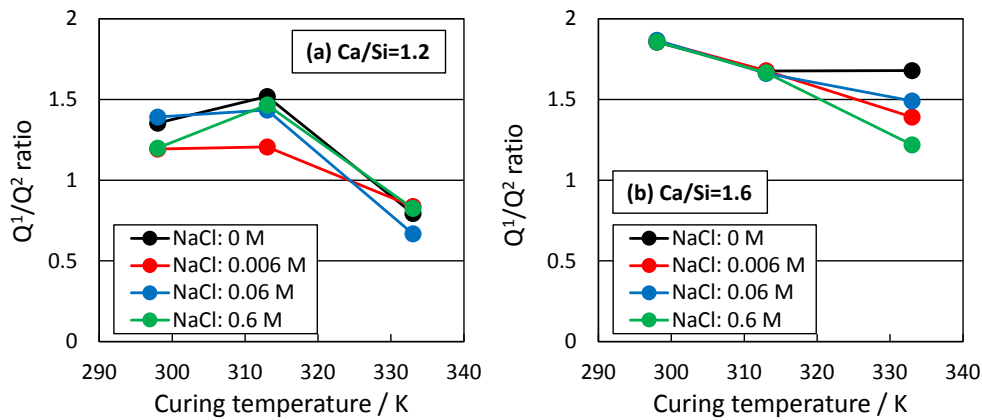


Fig. 9. Q^1/Q^2 ratio of CSH gel for the sorption of Cs/Ba ions. (Data for 298 K except for NaCl 0 M were taken from Saito et al. (2015)[1])

Q^0 (no siloxane bond). In consideration of the results shown in Fig. 5, the sorption of Cs increased with the depolymerization of the silicate chain. In other words, Cs ions are incorporated into CSH gel with the structural deformation.

From these results, under relatively high temperatures, such incorporation effect of CSH gel for cations will increase because of the facilitation of the structural deformation with increment of temperature. In the case of Ba ions as well as Cs ions, the sorption of Ba ions also remains relatively high by such incorporation effect even if the temperature increases. These chemical alterations of CSH gel occur under the condition saturated with groundwater. CSH gel formed under the condition saturated with groundwater rarely dries around the repository. Also, in the experiments, CSH gel was prepared and applied to the sorption experiments without the drying process for applicable simulation of the conditions after closure. Once CSH gel is dried and dehydrated, its chemical properties alter due to the loss of free water, although dried CSH gel is rehydrated. Considering that the condition saturated with groundwater around the repository remains in a temperature range up to 333 K, CSH gel formed as a secondary mineral will show the sorption of cationic radionuclides with the incorporation effect as mentioned above.

CONCLUSION

This study examined the influence of temperature on the interaction of Cs and Ba ions with CSH gel. The sorption of Cs ions on CSH gel increased and that of Ba ions remained relatively high even though the temperature increased up to 333 K. Furthermore, the results of Raman spectroscopy indicated the depolymerization of the silicate chain in CSH gel with the increase in temperature. These results suggest that the adsorption of cations increases with the structural deformation of CSH gel under the condition of higher temperature. In addition, the coexistence of Ba ions did not affect the adsorption of Cs ions on CSH gel. In the geological disposal system, CSH gel formed as a second mineral contributes to the retardation effect of the radionuclide migration, and such an effect is expected to occur under the geological temperature conditions around the repository.

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