

**Interactions of Cesium and Barium Ions with Calcium Silicate Hydrate under the Condition Saturated with Saline Water – 15247**

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**ABSTRACT**

The interaction of cesium (Cs) and barium (Ba) ions with calcium silicate hydrate (CSH gel) without drying processes was examined under the condition saturated with saline water, by monitoring the concentrations of Cs and Ba and using the Raman spectroscopy and the zeta potential. In the experiments, Ca/Si molar ratios of CSH gel were set to 0.4, 0.8, 1.2 and 1.6. Each sample was synthesized with CaO powder, SiO<sub>2</sub> powder and NaCl solution in given combinations. The concentration of NaCl solution was set to 0.006, 0.06 and 0.6 M. At the same time, CsCl or BaCl<sub>2</sub> solution was added to the sample in order to adjust its concentration to 1.0 mM. The curing period was set to 7, 14, 30 days. As a results, the sorption of Cs and Ba ions on CSH gel became stronger with lower Ca/Si molar ratio. On the other hand, even though the zeta potential showed the surface charge of higher Ca/Si ratio samples was positive charge which inhibits the sorption of cations, Cs and Ba ions significantly sorbed on CSH gel. In addition, Raman spectra of higher Ca/Si ratio samples showed that the degree of depolymerization of silicate chain increased with the sorption of Cs and Ba ions on CSH gel. In other words, even in higher Ca/Si ratio samples, Cs and Ba ions can sorb on CSH gel through the structural deformation of CSH gel. These results suggest that CSH gel might be able to contribute the migration retardation of Cs and/or Ba ions through the interaction with CSH gel, even if the near-field of the geological repository are saturated by saline groundwater.

**INTRODUCTION**

As in other countries, the geological repository of high level radioactive wastes (HLW) in Japan requires a large amount of cementitious materials for its construction [1]. Since cement pore water abundantly contains alkaline species such as sodium (Na), potassium (K) and calcium (Ca) ions, the leaching of pore water to surroundings would cause the alteration of groundwater up to 13 in pH around the repository system after backfilling [2]. Furthermore, such highly alkaline groundwater dissolves silicate minerals and forms Calcium-Silicate-Hydrate (CSH) gel with around 0.85 to 1.7 in Ca/Si molar ratio as a secondary mineral, which is predicted to be stable during a long time period exceeding one hundred thousand years [3]. That is, for a more reliable estimate of radionuclide migration, it is also necessary to comprehend various interactions between CSH gel and long life radionuclides (such as Cs-135, Am-241, Am-243 and Np-237). Of them, this study focused on the interactions of Cs ions (monovalent cations) with CSH gel, in comparison to those with Ba ions (divalent cations). Besides, saline groundwater might affect those interaction as compared with fresh groundwater. Therefore, in this study, the interactions of Cs and Ba ions with CSH gel under a condition saturated with saline water were examined by using CSH gel without drying process because the repository would be saturated again with the groundwater after backfilling.

## EXPERIMENTAL

### Samples

For observing the sorption behavior of Cs and Ba onto CSH gel samples, this study prepared CSH samples with the Ca/Si molar ratio set to 0.4, 0.8 1.2 and 1.6, under a condition saturated with nitrogen gas. The main procedure are the same as the previous work [4]. Table I shows the given ratios to synthesize each CSH gel sample with CaO, SiO<sub>2</sub>, and distilled water. SiO<sub>2</sub> (Fumed Silica, AEROSIL 300) was purchased from Japan AEROSIL Ltd. The specific surface area of BET (N<sub>2</sub> gas) was 300±30 m<sup>2</sup>/g. All of the other chemicals were purchased from Wako Pure Chemical Industries Ltd, and were used without further purification.

Table I. Materials used to synthesize sample [4].

Ca/Si ratio	CaO [g]	SiO <sub>2</sub> [g]	Solution [mL]
0.4	0.408	1.092	30
0.8	0.641	0.859	30
1.2	0.792	0.708	30
1.6	0.898	0.602	30

Table II summarizes the detail of CSH gel samples. In this study, the four types of CSH gel samples were prepared by the following procedures. (1): neither CsCl nor BaCl<sub>2</sub> solution is added to CSH gel sample (hereinafter referred to as “Cs/Ba-free sample”). (2): CsCl solution is added before curing the CSH gel (Cs-co-precipitation sample). (3): BaCl<sub>2</sub> solution is added before curing the CSH gel (“Ba-co-precipitation sample”). And (4): Both CsCl and BaCl<sub>2</sub> solution is added in co-precipitation sample (“Cs and Ba- co-precipitation sample”). In the sample of (2) or (3), the concentration of Cs or Ba ions, i.e., [Cs<sup>+</sup>] or [Ba<sup>2+</sup>] was set to 1.0 mM. Besides, in the sample of (4), [Cs<sup>+</sup>] and [Ba<sup>2+</sup>] were set to the same concentration, 0.5 mM. The concentration of NaCl solution of the sample used as simulated saline groundwater was set to 0.006, 0.06 and 0.6 M.

### Procedure

All samples were adjusted without drying process. The experimental procedure of this study followed the basic methods already reported by Furuya et al. [4] except the concentration measurements of Cs/Ba ions in the solution. In order to avoid contact with air, the synthesis of each sample was conducted in a glove bag filled with nitrogen gas. The sample tubes, of which volume was 50 mL, were sealed and constantly shaken with 120 strokes/min with the shaker attached a thermostat function. The temperature was kept constant within 298±1 K. The curing period of the sample was set to 7, 14, 30 days. After the above processes, CSH gel samples were centrifuged for 10 minutes at 7,500 rpm. Then, the liquid phase of CSH gel samples was filtered with 0.20 μm membrane filter. In the filtrated aliquot (liquid phase), the concentration of Cs ions was measured by Atomic Adsorption Spectrometry (Thermo Fisher Scientific, Inc., iCE 3000 series AA spectrometer), and the concentration of Ba ions was measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (Seiko Instruments Inc., SPS7800 Plasma Spectrometer). Besides, this study analyzed the polymerization degree of silicate chain in CSH gel by using a laser Raman spectrophotometer (JASCO, NRS-3300), which was equipped 532 nm YAG (Yttrium Aluminum Garnet) laser. Furthermore, the zeta potential of CSH gel was measured with adding

the aliquots of CSH gel from each sample tube into the same chemical component solution by Dynamic light scattering measurements (Otsuka Electronics Co., Ltd., ELSZ-2PLUS).

Table II. Conditions of CSH gel Samples.

Samples	Concentration of NaCl [M]	Ca/Si molar ratio	Curing time [days]	Concentration of ion [M]						
(1)Cs/Ba- free Samples	0.006, 0.06, and 0.6	0.4, 0.8, 1.2, and 1.6	7	[Cs <sup>+</sup> ]=0 [Ba <sup>2+</sup> ]=0						
			14							
			30							
(2)Cs- Co-precipitation Samples			0.006, 0.06, and 0.6	0.4, 0.8, 1.2, and 1.6	7	[Cs <sup>+</sup> ]=1.0 [Ba <sup>2+</sup> ]=0				
					14					
					30					
(3)Ba- Co-precipitation Samples					0.006, 0.06, and 0.6	0.4, 0.8, 1.2, and 1.6	7	[Cs <sup>+</sup> ]=0 [Ba <sup>2+</sup> ]=1.0		
							14			
							30			
(4)Cs/Ba- Co-precipitation Samples							0.006, 0.06, and 0.6	0.4, 0.8, 1.2, and 1.6	7	[Cs <sup>+</sup> ]=0.5 [Ba <sup>2+</sup> ]=0.5
									14	
									30	

## RESULT AND DISCUSSION

### Zeta potential

Fig. 1 shows the zeta potential of Cs/Ba- free samples. As shown in these results, the surface charge of higher Ca/Si ratio samples was positive charge which inhibits the sorption of cations under the condition saturated with saline water [5]. On the other hand, the surface charge of lower Ca/Si ratio was negative charge, which promotes the sorption of cations on CSH gel. In addition, the zeta potential did not depend on the NaCl concentration and the curing time.

### Amount of Cs and Ba in the Solid Phases

Fig. 2 shows the amount of Cs ions sorbed on the solid phases for each of Cs- co-precipitation samples. The amounts of Cs ions were calculated from a concentration of Cs ions in liquid phase and a volume of liquid phase. As shown in Figs. 2, the sorbed amount of Cs to CSH gel depended on the Ca/Si ratio [6], the NaCl concentration and the curing time. The sorption of Cs ions on CSH gel became stronger with lower Ca/Si molar ratio. Besides, the increase in the concentration of NaCl was decreased the amount of Cs ions sorbed on CSH gel. This means that the sodium ions inhibit the sorption of Cs ions on CSH gel. In addition, even in higher Ca/Si ratio samples of which surface charge is positive, the sorption of Cs ions on CSH gel underwent around 20 %. This results suggest that the sorption of Cs ions is not only due to electrostatical effect on the CSH gel.

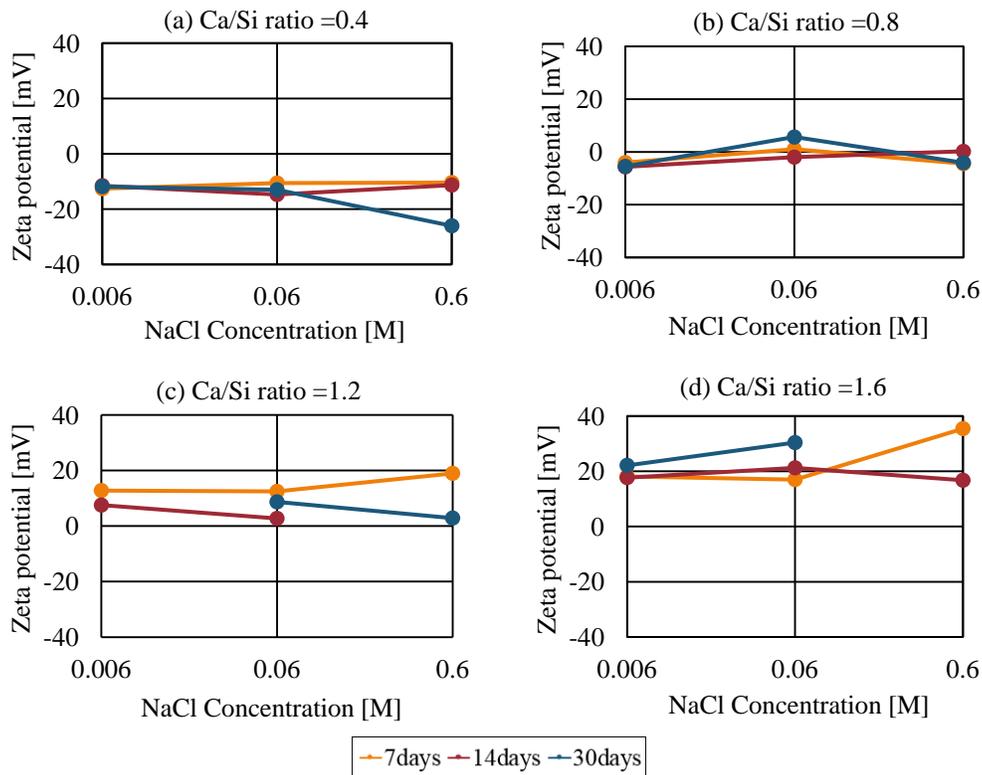


Fig. 1. Zeta potential of Cs/Ba- free Samples.

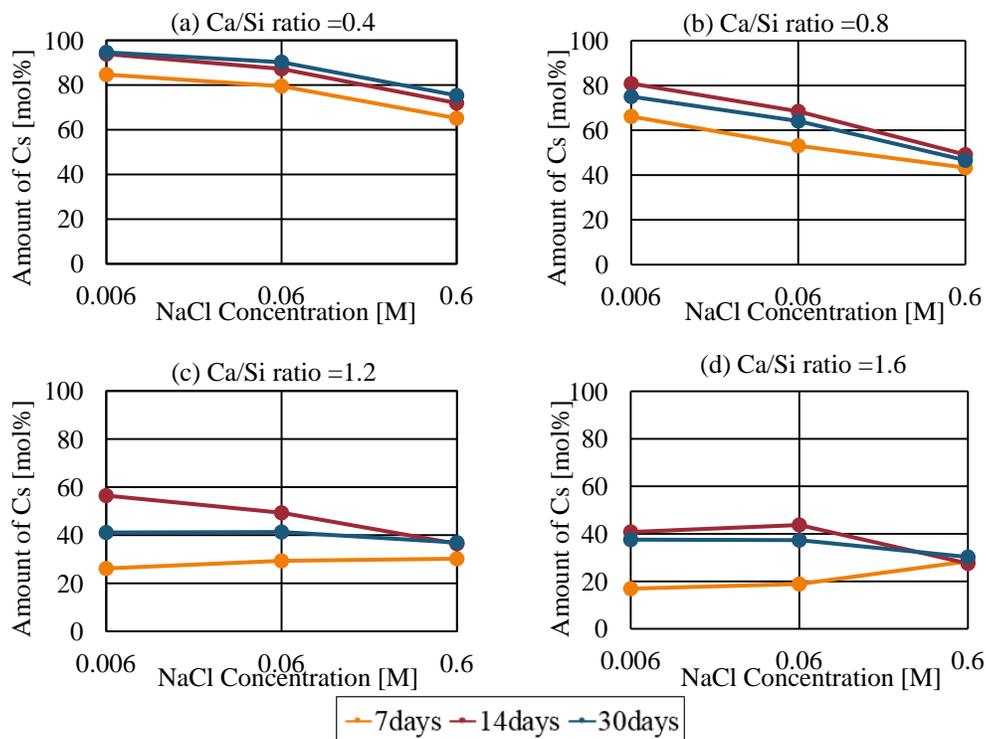


Fig. 2. Amount of Cs ions sorbed on the solid phases for Cs- Co-precipitation Samples.

Fig. 3 shows the amount of Ba ions sorbed on the solid phases each of co-precipitation samples. As shown in Figs. 3, the sorbed amount of Ba to a solid phase also depended on the Ca/Si ratio and the NaCl concentration. Furthermore, the sorption amount of Ba ions (divalent cation) apparently exceeded that of Cs ions.

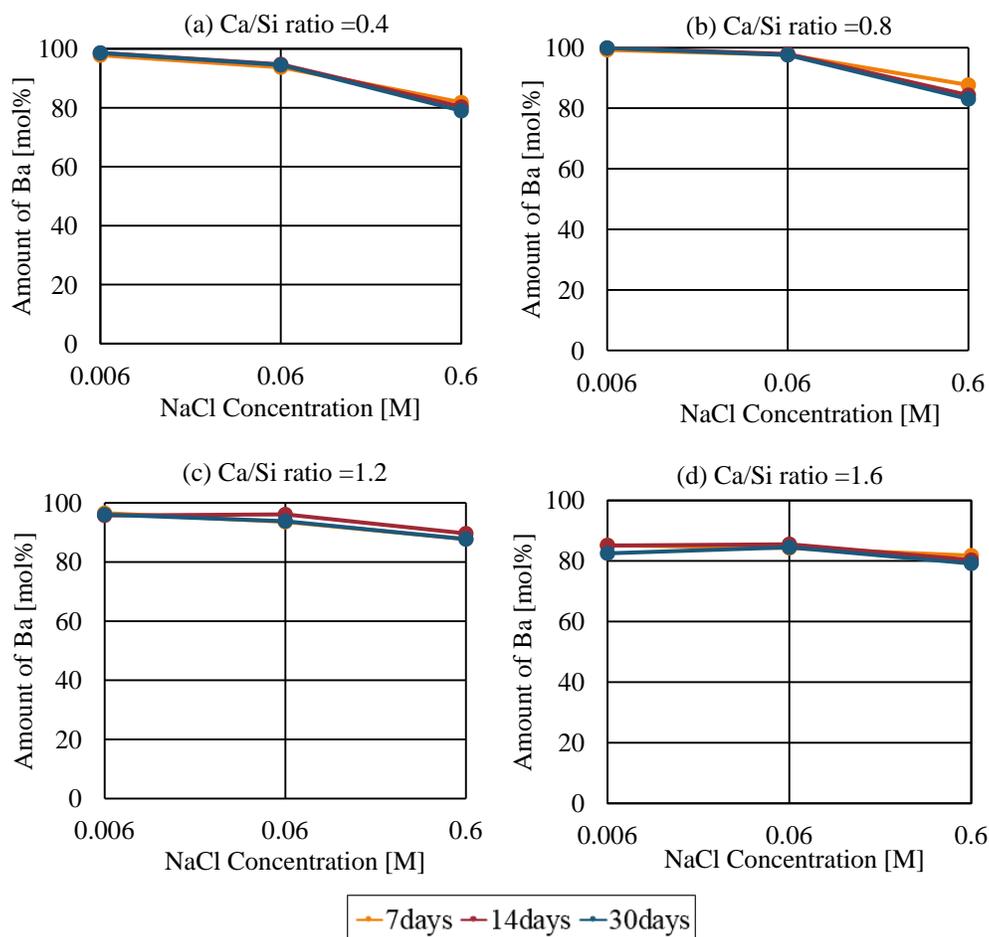


Fig. 3. Amount of Ba ions sorbed on the solid phases for Ba- Co-precipitation Samples.

Figs. 4 and 5 show the amounts of Cs and Ba ions sorbed on the solid phases after curing each of Cs/Ba-co-precipitation samples. As shown in these figures, the sorbed amount of Cs to CSH gel was not influenced by Ba ions which is coexistent ions, and vice versa.

Through the whole sorption experiments, even in higher Ca/Si ratio samples such as Ca/Si=1.6 which surface charge is positive and under the condition of 0.6 M NaCl, Ba ions on CSH gel underwent 80 % of the initial concentration. Also, in the case of Cs ions, more than about 20% of the initial concentration sorbed under the various conditions in spite of the positive charge of the solid surface. These results suggest that the sorption of Cs and Ba ions on CSH gel cannot be explained by only electrostatic reactions.

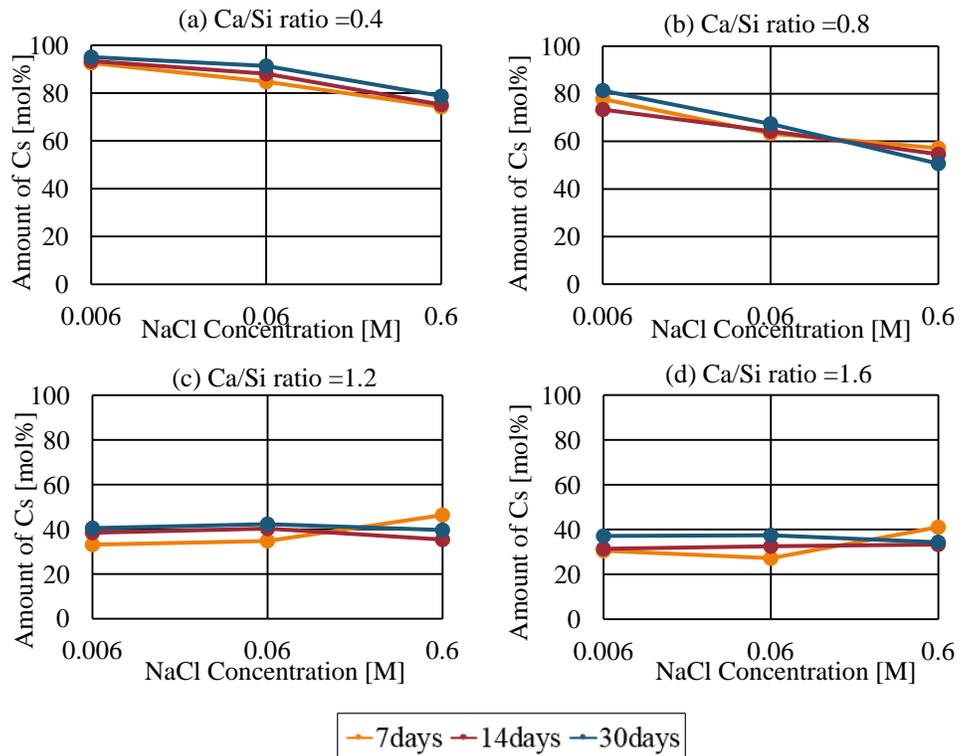


Fig. 4. Amount of Cs ions sorbed on the solid phases for Cs/Ba- Co-precipitation Samples.

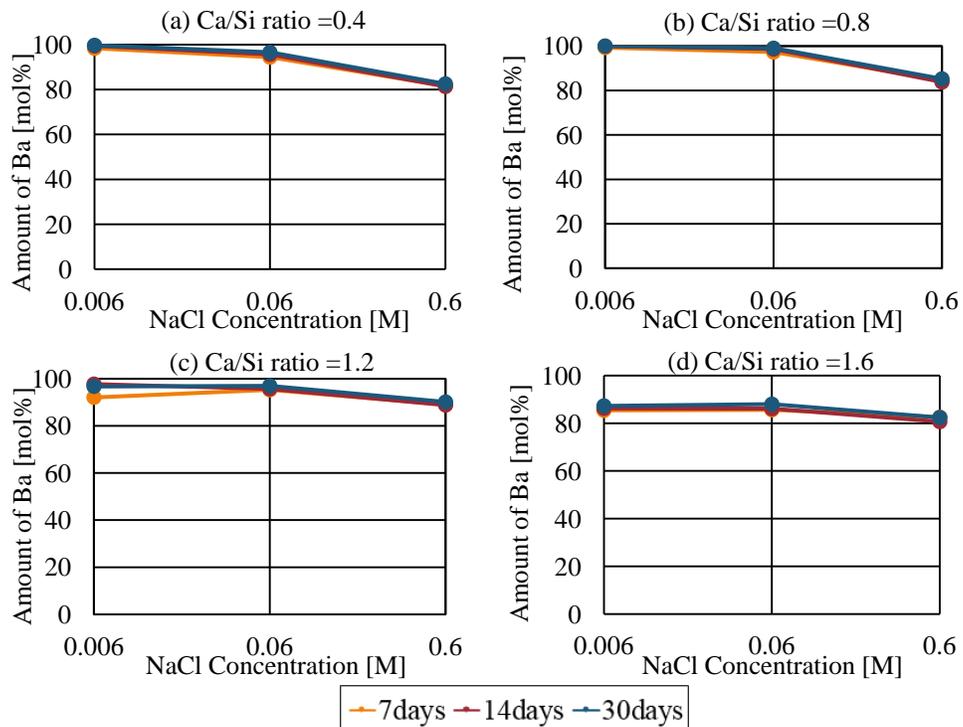


Fig. 5. Amount of Ba ions sorbed on the solid phases for Cs/Ba- Co-precipitation Samples.

## Raman Spectra

From the results of the amount of Cs and Ba ions sorbed into solid phase of CSH gel and zeta potential measurement, the sorption mechanism of Cs and Ba ions on CSH gel seems very complicated. These suggest that not only electrostatic reactions but also the change in the structure of CSH gel might affect the sorption of Cs and Ba ions. Accordingly, this study obtained Raman spectrometry to examine the structure of CSH gel.

So far, many studies have reported that the structure of CSH gel is mostly similar to tobermorite [7, 8]. The primary structure of tobermorite consists of silicate chain and CaO layer. The silicate chain is located in the interatomic spacings of Ca-O layer. The silicate chains of  $\text{SiO}_4$  tetrahedrons is generally expressed as  $\text{Q}^n$ , where “n” of  $\text{Q}^n$  is the number of siloxane bond of  $\text{SiO}_4$  tetrahedrons. The peak position of Raman spectra of  $\text{SiO}_4$  tetrahedrons strongly depends on the number of “n”. This study especially focused on the peak of symmetric stretching vibration of  $\text{Q}^1$  ( $870\text{ cm}^{-1}$ ) and  $\text{Q}^2$  ( $1010\text{ cm}^{-1}$ ) [4].

Fig. 6 shows  $\text{Q}^1/\text{Q}^2$  intensity ratio of Cs/Ba-free sample. While in low Ca/Si ratio samples (Ca/Si=0.4 and 0.8) the peak of symmetric stretching vibration of  $\text{Q}^1$  were not detected, the peak for high Ca/Si ratio samples (Ca/Si=1.2, 1.6) could be detected. The previous study also reported that the intensity of  $\text{Q}^1$  peak becomes stronger with higher Ca/Si ratio [9]. In this study,  $\text{Q}^1/\text{Q}^2$  intensity ratios were applied as an indicator of the depolymerization of the silicate chain. That is, when  $\text{Q}^1/\text{Q}^2$  intensity ratio of a CSH gel sample is higher, the silicate chain of the CSH sample is more depolymerized.

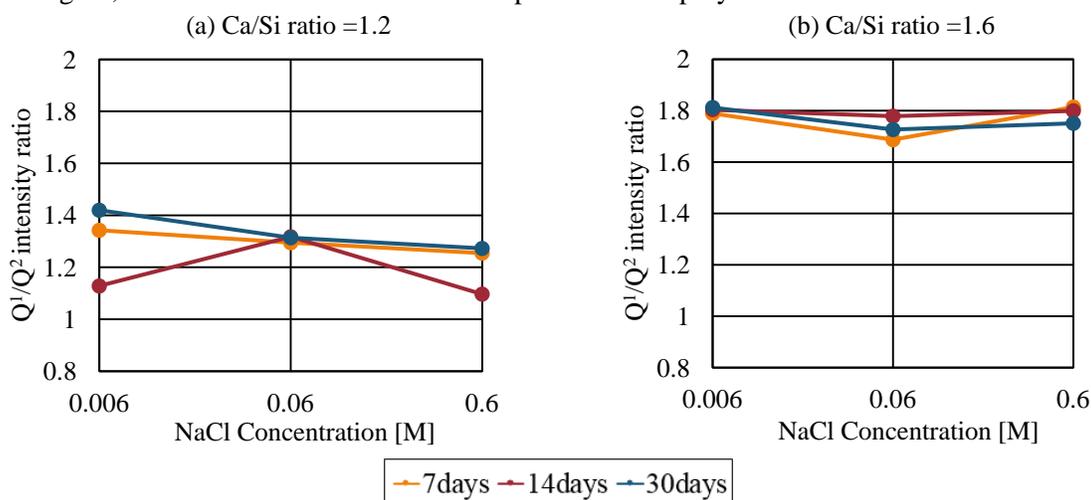


Fig. 6.  $\text{Q}^1/\text{Q}^2$  ratio of Cs/Ba- free Samples.

Figs.7, 8 and 9 show the  $\text{Q}^1/\text{Q}^2$  intensity ratios of co-precipitation samples. The CSH gel sorbing Ba ions deforms its structure much more than that of Cs ions. This means that Ba ions, which Stokes radius is larger than Cs ions, remarkably affect the structural transformation of CSH gel. In other words, even in higher Ca/Si ratio samples, Ba ions can sorb on CSH gel through the structural deformation of CSH gel. Such a tendency strongly appears compared to CSH gel sorbing Cs ions.

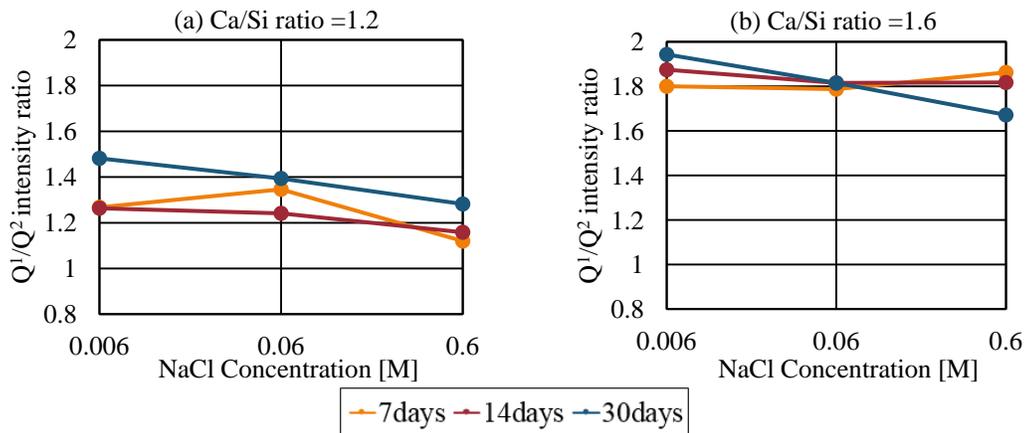


Fig. 7.  $Q^1/Q^2$  ratio of Cs- Co-precipitation Samples.

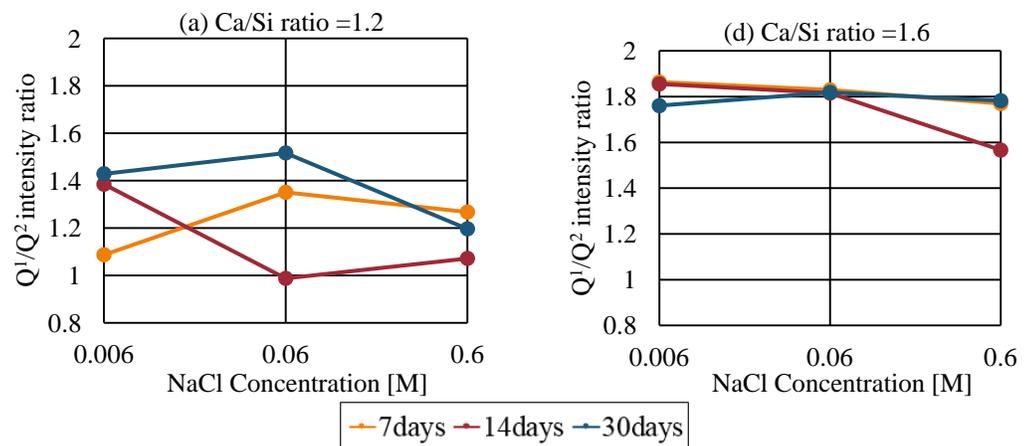


Fig. 8.  $Q^1/Q^2$  ratio of Ba- Co-precipitation Samples.

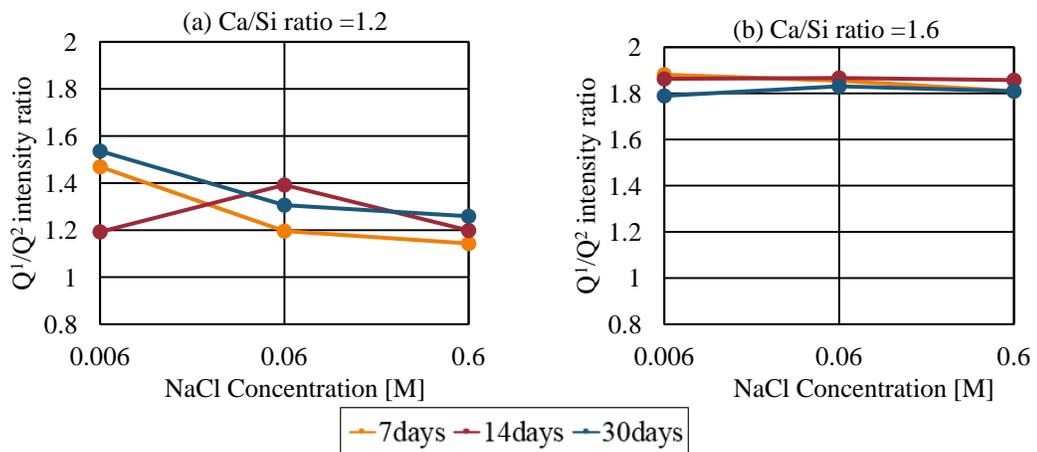


Fig. 9.  $Q^1/Q^2$  ratio of Cs/Ba- Co-precipitation Samples.

## CONCLUSIONS

In this study, the interaction of Cs and Ba ions with CSH gel without drying process was examined by measuring the concentrations of Cs and Ba, the Raman spectra and the zeta potential. The results showed that the sorption amounts of Cs and Ba ions on CSH gel became stronger with lower Ca/Si molar ratio. And the sorption amount of Ba ions which is divalent cation was apparently more than that of Cs ions. Besides, the increase in the concentration of NaCl decreased the amount of Cs and Ba sorbed on CSH gel. This means that the sodium ions inhibit the sorption of Cs and Ba ions on CSH gel.

On the other hand, the zeta potential measurement showed the surface charge of higher Ca/Si ratio samples was positive charge which inhibits the sorption of cations. However, even under any conditions with Ca/Si ratio higher than 1.2 (up to 0.6 M in Na ions concentration), Ba ions on CSH gel underwent 80 % of the initial concentration in this study. Also, in the case of Cs ions, more than about 20% of the initial concentration sorbed. The results suggested that the sorption of Cs and Ba ions cannot be explained only by electrostatic reactions. Furthermore, the Raman spectra from higher Ca/Si ratio samples showed that the degree of depolymerization of silicate chain increased with the sorption of Cs and Ba ions on CSH gel. In other words, even in higher Ca/Si ratio samples, Cs and Ba ions can sorb on CSH gel through the structural deformation of CSH gel.

From these results, CSH gel might be able to contribute the migration retardation of Cs ions through the interaction with CSH gel, even if the near-field of the geological repository are saturated by saline groundwater. Since Cs-135 undergoes beta decay ( $\beta^-$ ) with the half-life of 2.3 million years producing Ba-135, this study would also provide a fundamental base to estimate Cs-135 migration in the coexisting system of Ba ions with CSH gel.

## REFERENCES

1. JNC (Japan Nuclear Cycle development institute), "H12 Project to Establish the Scientific and Technical Basis for HLW Disposal in Japan," Vol. 2, JNC TN1400 99 (1999).
2. G. B. Alexander, W. M. Heston, R. K. Iler "The solubility of Amorphous Silica in Water", THE JOURNAL OF PHYSICAL CHEMISTRY, **58**, 453 (1954).
3. G. M. N. Baston, A. P. Clacher, T. G. Heath, F. M. I. Hunter, V. Smith, S. W. Swanton, "Calcium silicate hydrate (C-S-H) gel dissolution and pH buffering in a cementitious near field", Mineralogical Magazine, **76**, 3045 (2012).
4. J. Furuya, T. Chida, Y. Niibori, H. Mimura, "Raman Spectra of Calcium Silicate Hydrates Sorbing Iodine Ions in Saline Groundwater," Proceedings of WM2014 Conference, Phoenix, USA, March 2-6, Paper No. 14077 (2014).
5. T. Fujita, D. Sugiyama, S. W. Swanton, B. J. Myatt, "Observation and characterization of colloids derived from leached cement hydrates", Journal of Contaminant Hydrology, **61**, 3 (2003).
6. H'el'ene Viallis-Terrisse, Andr'e Nonat, Jean-Claude Petit, Catherine Landesman, C'ecile Richet, "Specific interaction of cesium with the surface of calcium silicate hydrates", Radiochimica Acta, **90**, 699 (2002).
7. T. Iwaida, S. Nagasaki, S. Tanaka, T. Yaita, S. Tachimori, "Structure alteration of C-S-H (calcium silicate hydrated phases) caused by sorption of caesium," Radiochimica Acta **90**, 677 (2002).
8. G. Richardson, "The calcium silicate hydrates", Cement and Concrete Research **38**, 137 (2008).
9. Jung J. Kim, Emmy M. Foley, Mahmoud M. Reda Taha, "Nano-mechanical characterization of synthetic calcium-silicate-hydrate (C-S-H) with varying CaO/SiO<sub>2</sub> mixture ratios", Cement & Concrete Composites **36**, 65 (2013).

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