

## **Sorption Behavior of Cesium Ions on Calcium Aluminosilicate Hydrate under the Condition Saturated with Saline Water– 17096**

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### **ABSTRACT**

This study focused on the interaction of cesium (Cs) ions with calcium silicate hydrate (CSH) and calcium aluminosilicate hydrate (CASH) gel, of which sorption effect may retard the migration of Cs ions in the radioactive waste disposal system. In the sorption experiments, the influences of the Al/Si molar ratio of C(A)SH and the curing periods on the sorption of Cs ions into C(A)SH under the saline conditions were examined without drying processes by monitoring the concentrations of Cs, Ca, Si and Al. Besides, Raman spectroscopy were applied to the structure analysis of C(A)SH. As a result, the sorption of Cs ions on C(A)SH became larger with the increase in the Al/Si molar ratios under the all conditions. Furthermore, Raman spectra showed the formation of Al-tetrahedrons and Al-octahedrons, and the increase in the polymerization degree of silicate chain in CASH with adding Al. These results mean that the negative layer-charge of the sheets containing Si- and Al-tetrahedrons and Al-octahedron will accelerate the sorption of Cs ions of positive charge, electrostatically.

### **INTRODUCTION**

Radioactive wastes by the accident of Fukushima nuclear power plant contain radioactive Cs-137. Some parts of these wastes will be solidified with cementitious materials as a form of their final disposal body. For assessing the migration of Cs-137, it is important to comprehend the sorption of Cs-137 on cementitious materials. Typically, the main component of cementitious materials is calcium silicate hydrate (CSH) [1]. The authors in a previous study [2] showed a stronger sorption of Cs ions into CSH than that into a host rock such as granite. Since CSH is a main component of cement, the cement used for the construction of the repository might retard the migration of Cs. Besides, recent cement tends to contain more aluminum (Al) because the amount of blast-furnace slag fine powder mixed into cement clinker becomes larger in order to reduce the environmental loads and improve the durability of cementitious materials [3, 4]. Paradal et al. [5] reported that such cementitious composition forms not only CSH but also calcium aluminosilicate hydrate (CASH) taken Al in its structure. Therefore, this study examined the interaction of CASH and Cs which might affect the migration of radionuclides released from the repository. Moreover, high-level radioactive wastes (HLW) contain the radioactive cesium (Cs-135) of which half-life is 2.3 million

years. The geological disposal system for HLW also needs a large amount of cementitious materials for constructing the repository. By the alteration of host rock with leaching cementitious components, CSH and CASH forms as secondary minerals around the repository. Such CSH and CASH also may retard the migration of Cs-135 by the sorption effect. So far, in particular, the sorption of Cs on CASH has been hardly discussed. On the other hand, some previous studies have reported the sorption behavior of Cs ions to CSH. However, most experiments dried CSH samples once, even if the underground environment is saturated with groundwater after the closure of the repository [6]. Therefore, this study examined the sorption behavior of Cs ions on CASH without drying processes in the presence of NaCl for also considering an underground condition saturated with saline groundwater.

## EXPERIMENTAL METHODS

The sorption experiments using C(A)SH gel followed the basic procedures reported in previous studies used CSH only [2, 7]. In the experiments, each sample of CASH or CSH (Al free) was synthesized by mixing CaO, fumed silica (AEROSIL 300 purchased from Japan AEROSIL Ltd.), and aluminum nitrate with a NaCl solution. All reagents except for fumed silica were purchased from Wako Pure Chemical Industries Ltd. At the same time, a CsCl solution was added to the sample in order to adjust the concentration of Cs ions (nonradioactive) to 1.0 mM. The concentrations of NaCl were set to 0, 0.006, 0.06, 0.6 M. The preparation processes were conducted in a glove bag filled with nitrogen gas until the caps of sample tubes were closed. Ca/Si molar ratio of CSH and CASH was set to 1.6. The molar ratios of Al/Si were also set to 0, 0.125, 0.25, 0.375 and 0.5. ("Al/Si=0" means the formation of CSH.) Table 1 showed the measured weights of samples. The curing period was set to 7, 14, 28 days through considering that the concentrations of Si and Ca ions in liquid phase of CSH samples reach equilibrium concentrations within 7 days in our previous studies [8] and that the curing period for the strength test is set to 28 days after placing the concrete in Japan [9]. The initial Liquid/Solid ratio was adjusted to 20 mL/g, and the total volume of liquid phase was 30 mL. In the curing period, the samples were shaken with 120 strokes/min at 298 K in a thermostat. After curing, the solid (CASH or CSH) and liquid phase were separated by centrifuging at 7500 rpm for 10 minutes and filtrating with 0.20  $\mu\text{m}$  membrane filter. The concentrations of Ca, Si and Al ions in liquid phase were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (SPS7800, Seiko Instruments Inc.) and the Cs was measured by Atomic Adsorption Spectrometry (iCE 3000 series AA spectrometer, Thermo Fisher Scientific Inc.). The Raman spectroscopy (NRS-3300QSE, JASCO), of which excitation laser was 532 nm of YAG laser, was used to analyze the polymerization degree of silicate chain and the formation of Al-tetrahedrons or octahedrons of the solid phase as described later. As shown in Table 1, the contents of Al in the experiments were set up to 0.5 in Al/Si molar ratio. For such higher ratio of Al/Si, the structure of these CASH samples might not form homogeneously. However, this study defined these samples as "CASH" for assuming that the secondary minerals including Ca, Si and Al will form with the wide range of their ratios around the repository, while some

previous studies reported that, under the condition of 10 mol % of Al, secondary phases such as strätlingite ( $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 8\text{H}_2\text{O}$ ) were formed in advance of the CASH formation [10, 11].

Table 1. Measured weight of solid samples. (Total weight: 1.5 g)

Al/Si molar ratio	CaO (g)	SiO <sub>2</sub> (g)	Al(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O (g)
0	0.898	0.602	0.000
0.125	0.684	0.458	0.358
0.25	0.552	0.370	0.578
0.375	0.463	0.310	0.727
0.5	0.399	0.267	0.834

## RESULTS AND DISCUSSION

### Structural alteration of C(A)SH

Figs. 1, 2 and 3 show the fractions of Ca, Si and Al in solid phase to the initial amount respectively after 28 days. As shown in these results, the amount of Ca in solid phase (C(A)SH) decreased with the increase in Al/Si ratio while most of Si and Al added at the preparation were incorporated in solid phases. Calculating from these data, the Ca/Si molar ratio of the solid phase was close to 1.0 (initial value: 1.6) at Al/Si = 0.5. This means that Ca is excess in these systems.

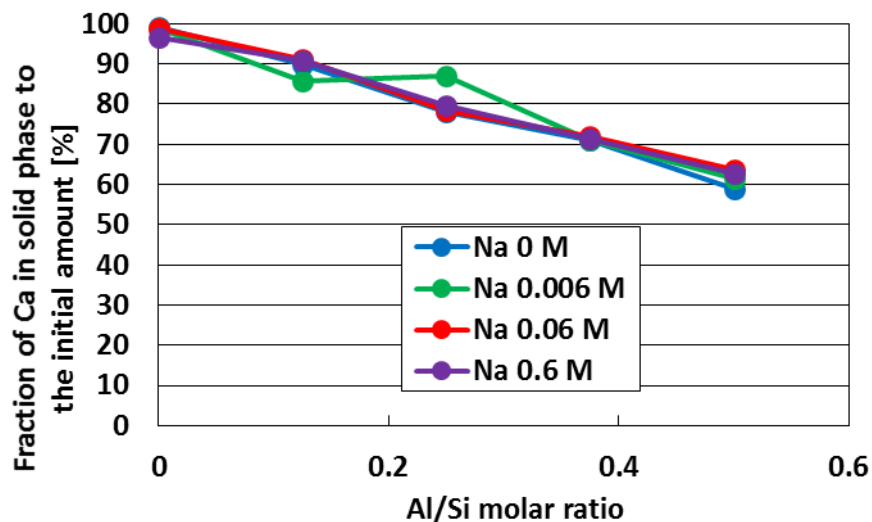


Fig. 1. Fraction of Ca in solid phase to the initial amount (28 day later).

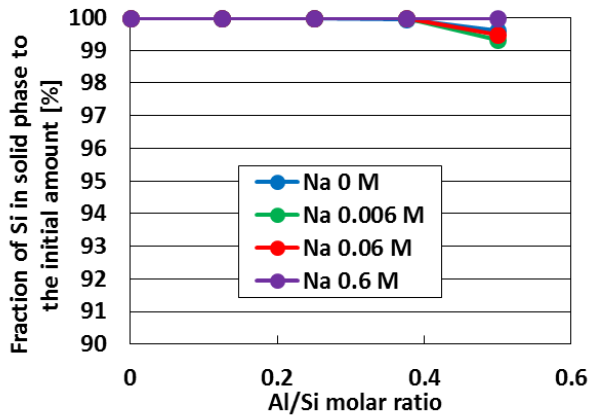


Fig. 2. Fraction of Ca in solid phase to the initial amount (28 days later).

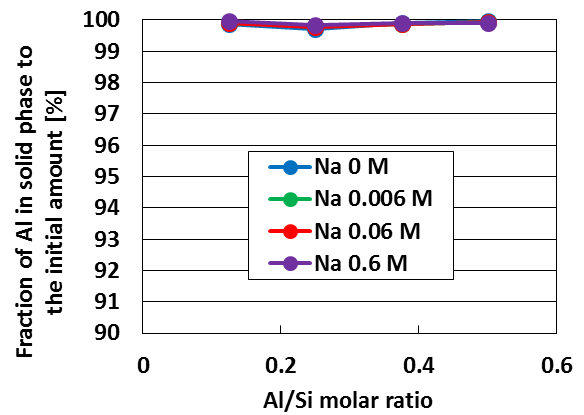


Fig. 3. Fraction of Ca in solid phase to the initial amount (28 days later).

Figs. 4 and 5 show the changes in the weight of liquid phase and solid phase after 28 days. As the Al/Si molar ratio became larger, the weight of liquid phase increased in Fig. 4, while the weight of solid phase decreased in Fig. 5. These results indicate the structural alternation of C(A)SH including possibility generating several phases. In addition, these changes in Figs. 1-5 were almost the same as those for 7 days and 14 days. This means that the hydration of C(A)SH and the concentrations of chemical species in liquid/solid phase will reach an equilibrium condition until 7 days.

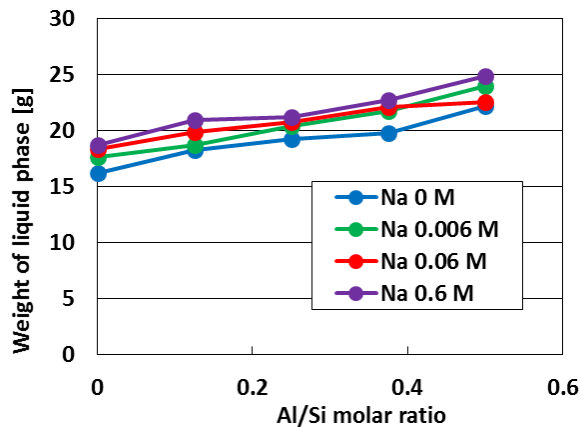


Fig. 4. Change in the weights of liquid phase (28 days later).

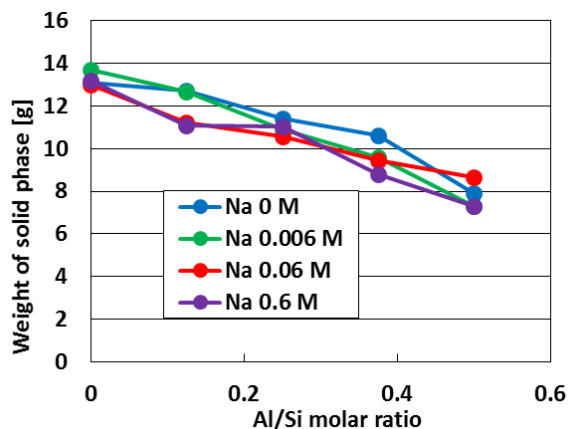


Fig. 5. Change in the weights of solid phase (28 days later).

Concerning the structure of CSH, Richardson [12] provided the approvable structure-model for CSH on the basis of the assumption that CSH gel is structurally similar to tobermorite consisting of a hydrated Ca-O layer between silicate chains. On the other hand, the structure of pure CASH gel has Al-tetrahedrons in silicate chains by the Si-Al substitution in CSH as reported by Pardal, et al.[5]. In this study, the degree of these silicate chains and the substitution of Al were observed

by Raman analysis. Fig. 6 shows Raman spectra for the C(A)SH samples (Al/Si = 0, 0.125, 0.25, 0.375, 0.5) under the condition of 0.06 M NaCl after 14 days. Those for other conditions in these experiments were almost the same as the results in Fig. 7. In Fig. 7, some peaks caused the structure of C(A)SH were detected. For the spectrum of Al/Si=0 in Fig. 7, the peaks of symmetric stretching vibration of  $Q^1$  ( $870\text{ cm}^{-1}$ ) and  $Q^2$  ( $1010\text{ cm}^{-1}$ ) were observed. Here, these peaks of  $Q^n$  express the polymerization degree of the  $\text{SiO}_4$  tetrahedrons in these silicate chains, where “n” is the number of bridging oxygen atoms (siloxane bond, Si-O-Si). For example,  $Q^2$  denotes that one  $\text{SiO}_4$  tetrahedron connects with the other two  $\text{SiO}_4$  tetrahedrons by two siloxane bonds. However, such peaks of  $Q^1$  and  $Q^2$  were not observed for the conditions of Al/Si=0.125 - 0.5. For the spectrum of Al/Si=0.125 - 0.5 in Fig. 7, the peaks of  $Q^3$  ( $1040\text{ cm}^{-1}$ ), Al-tetrahedron ( $710\text{ cm}^{-1}$ ) and Al-octahedron ( $520\text{ cm}^{-1}$ ) were observed. These suggest that the incorporation of Al to CSH will progress the polymerization of  $\text{SiO}_4$  tetrahedron sheet with the increase in Al-tetrahedron and Al-octahedron. In addition, the samples for the higher Al/Si ratios may be similar to some aluminosilicate minerals such as clay, for example muscovite [13], rather than CASH defined by cement chemistry.

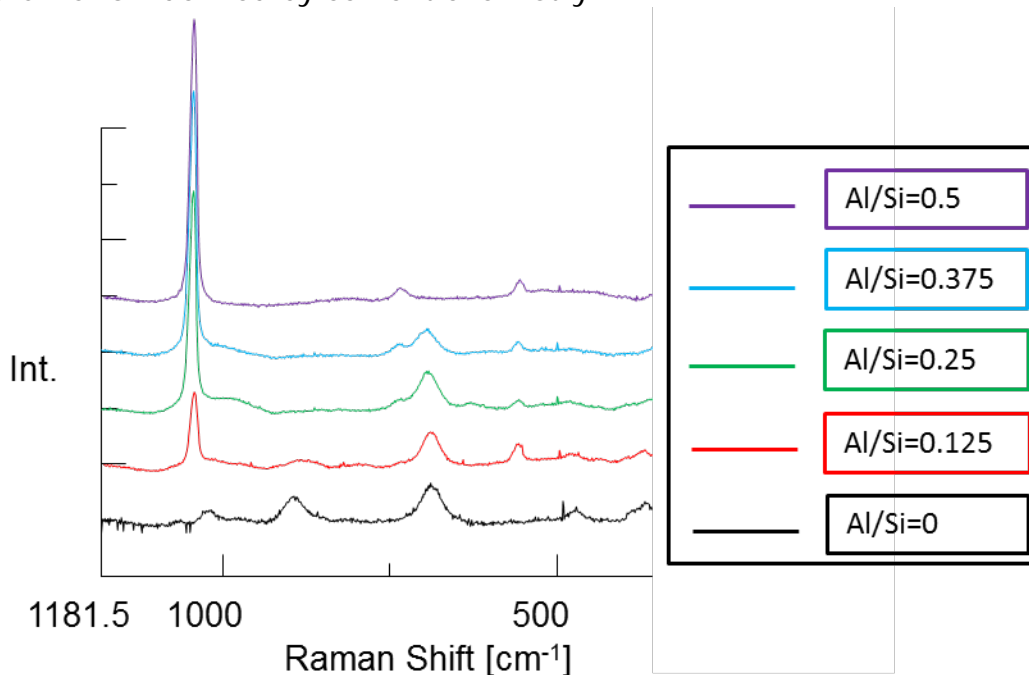


Fig. 6. Raman spectra of C(A)SH. (NaCl=0.06 M, 14 days later)

### Sorption of Cs ions on C(A)SH gel

Figs. 7, 8 and 9 show the sorption behaviors of Cs ions at 7, 14 and 28 days respectively. The vertical axis is the sorption amount of Cs per the weight of solid phase, considering the change in the weight of liquid phase and the solid phase after curing as shown in Figs. 4 and 5. As shown in Figs. 7-9, the sorption amount of Cs on C(A)SH became larger with the increase in Al/Si molar ratio. In general, many clay minerals adsorb cations so much because Al-tetrahedron and Al-

octahedron incorporated in the clay minerals make the layer charge negative. As described above, the Raman spectra of the samples adding Al in Fig. 7 showed the formation of Al-tetrahedron and Al-octahedron. Thus, the increase in the sorption of Cs ions for the higher Al/Si ratios in Figs. 7-9 will also reflect such electrostatic interaction in the layer sheets of CASH samples. Regarding the effects of Na ions on the sorption behavior of Cs, under the condition of the higher Al/Si ratio, the sorption amount of Cs roughly decreased with the increase in the Na concentration and the curing period. In Fig. 9, the decrease in the sorption of Cs was clear under the condition of 0.06 M NaCl or more. This means that excessive Na ions will inhibit the sorption of Cs ions on CASH though the electrostatic sorption of Cs ions is usually stronger than that of Na ions in consideration of their ionic radius. On the other hand, for the lower Al/Si molar ratios (specifically Al/Si=0.125), the influence of Na concentration on the sorption of Cs ions was not confirmed clear. Myers et al. [14] reported that CNASH ("N" means Na) is also formed in the condition of these lower Al/Si ratios by incorporating Na ions. Under such a condition, the formation of CNASH will more complicate the sorption behavior of Cs ions on C(A)SH, in addition to the competition with Na ions and the electrostatic interaction causing the layer charge. At least, in Fig. 9 for 28 days of the curing period, the sorption of Cs ions hardly changed except for the condition of 0.6 M NaCl accompanying excessive Na ions. Therefore, the influence of the CNASH formation on the sorption of Cs ions may be not large under the condition of up to 0.06 M of NaCl concentration. As a remarkable point, Cs ions significantly sorbed into C(A)SH even in the presence of excessive Na ions such as 0.06 M or more. This suggests that C(A)SH incorporates Cs ions with the high selectivity.

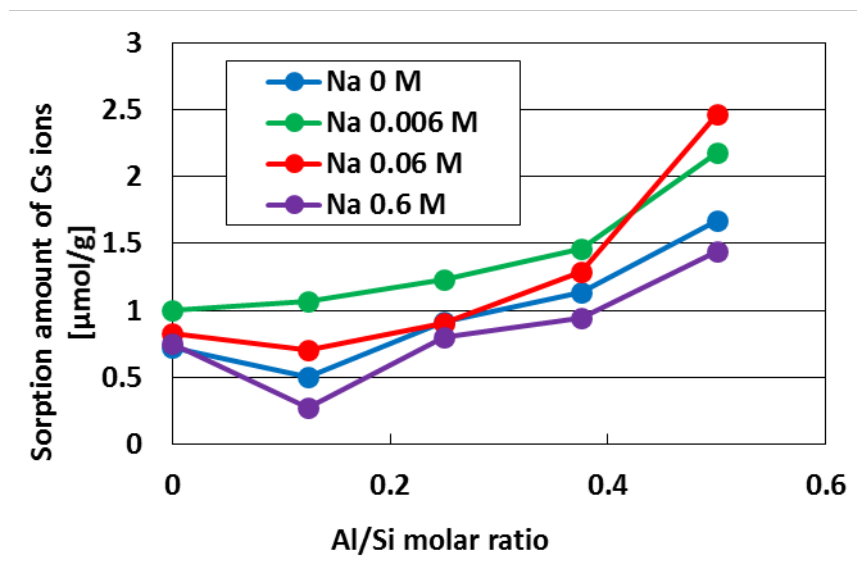


Fig. 7. Sorption of Cs ions (7 days later).

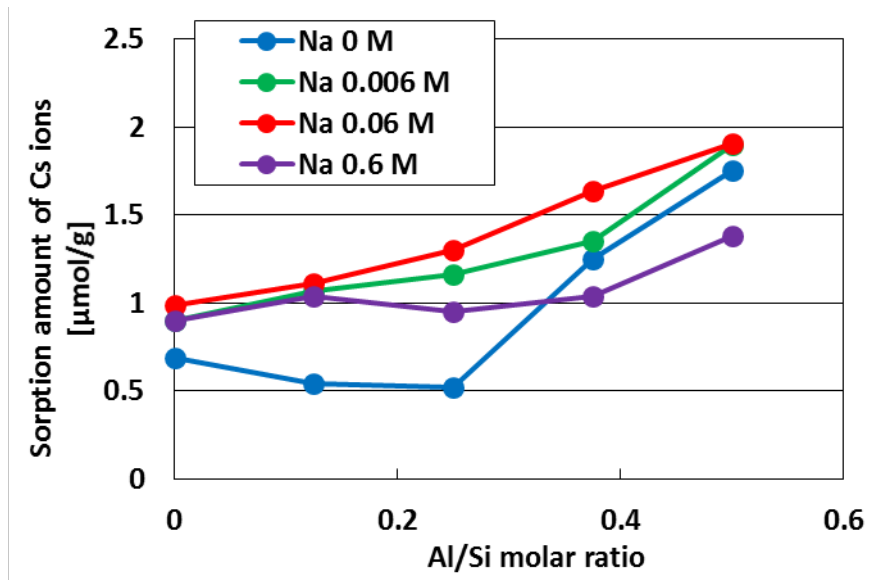


Fig. 8. Sorption of Cs ions (14 days later).

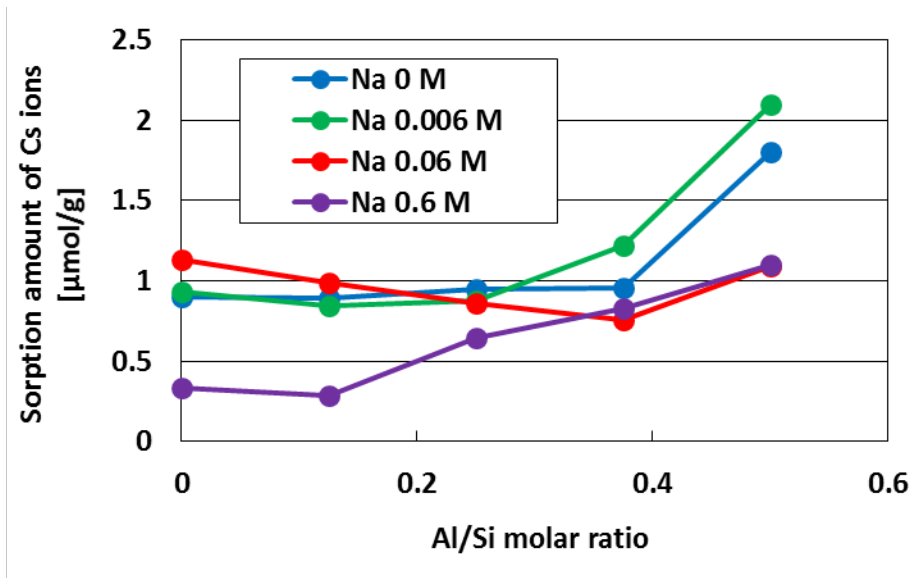


Fig. 9. Sorption of Cs ions (28 days later).

As mentioned in Fig.1, the evaluated amounts of Ca in solid phase after curing were different from the initial condition of 1.6 in Ca/Si molar ratio. For correcting this change in the amount of Ca in solid phase, Figs. 7, 8 and 9 were rewritten to Figs. 10, 11 and 12. Here, the horizontal axis of Ca/(Si+Al) molar ratio of solid phase was calculated by using really measured amount of Ca, Si and Al in solid phase. This notation also means the charge balance of the calcium anion ( $\text{Ca}^{2+}$ ) and the negative layer (Si and Al) in CASH. From the results in Figs. 10-12, it is confirmed that the sorption behavior of Cs on C(A)SH increase with decrease of the Ca ratio.

As mentioned above, the sorption of Cs ions on C(A)SH became larger with the increase in the Al/Si molar ratios, though the influence of the Na concentration is

not clear very much. This result suggests that CASH undergoes larger potential of Cs sorption than CSH, as a cementitious material or as a secondary mineral around the repository. That is, CASH also might play an important role for retarding the migration of Cs around the repository.

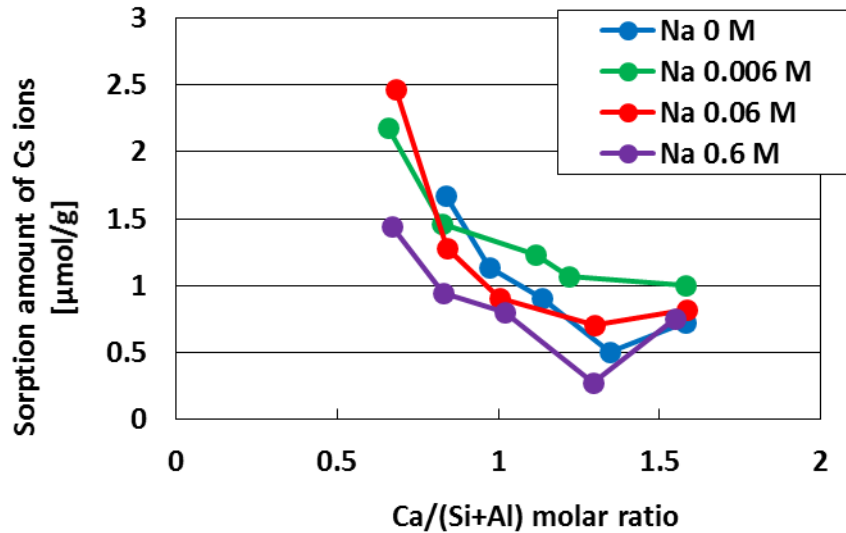


Fig. 10. Sorption of Cs ions as a function of Ca/(Si+Al) molar ratio (7 days later).

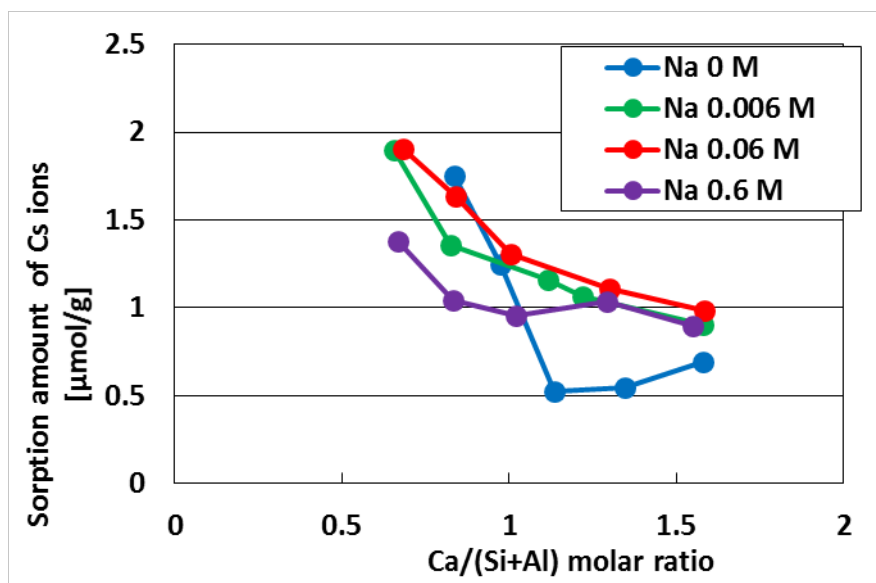


Fig. 11. Sorption of Cs ions as a function of Ca/(Si+Al) molar ratio (14 days later).



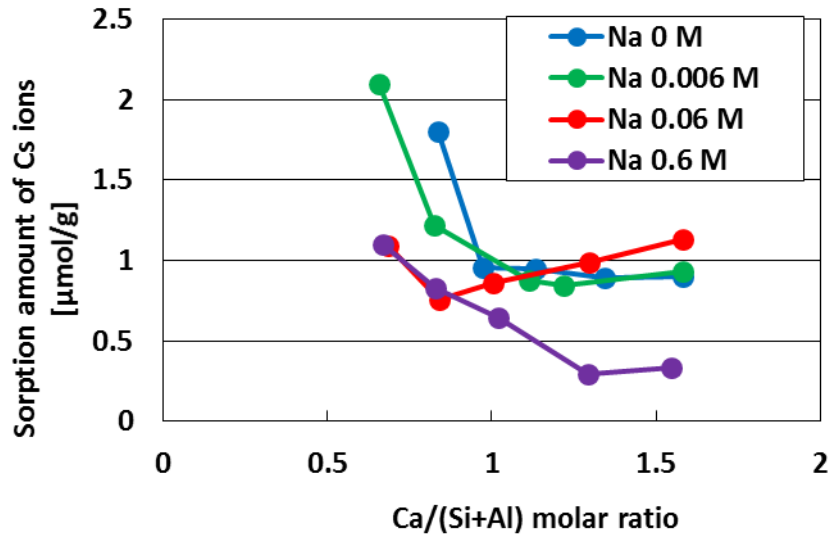


Fig. 12. Sorption of Cs ions as a function of Ca/(Si+Al) molar ratio (28 days later).

## CONCLUSIONS

This study examined the influence of the Al/Si ratio, the saline condition and the curing period on the interaction of Cs ions and CASH. As a result, the sorption of Cs ions on CASH increased with the increase in the Al/Si ratio for all conditions of NaCl concentration and the curing period. Besides, the results of Raman spectroscopy showed the formation of Al-tetrahedron, Al-octahedron and Q<sup>3</sup> with the incorporation of Al. In other words, the tetrahedral and octahedral sheets charged negative are formed in CASH. Such structural changes will contribute the increase in the sorption of cations such as Cs ions. While the sorption of Cs ions on CASH apparently became small with NaCl concentration of more than 0.06 M, Cs ions significantly sorbed into CASH. These results suggest that CASH, formed in cementitious materials or as secondary minerals around the repository, will retard the migration of Cs ions even if the underground environment are saturated by saline water with the wide range of NaCl concentration.

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