**Sorption Behavior of Iodide Ions on Calcium Silicate Hydrate
Formed under the Condition Saturated with Saline Water − 17069**

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ABSTRACT

The sorption behavior of iodide ions on calcium-silicate-hydrate (CSH gel) under the condition saturated with saline water was examined by using a Raman spectroscopy and ICP-AES, without drying process. In the sorption experiments, I-127 is a stable isotope was used as an alternative of I-129. CSH gel was synthesized with mixing CaO, SiO_2, and NaCl solution. The Ca/Si molar ratios of CSH gel were set to 0.4, 0.8, 1.2 and 1.6, and the concentration of NaCl solution was set to 0.6 M for simulating the condition of saline groundwater. The liquid/solid weight ratios of CSH gel were set to 10, 13, 15, 17, and 20, and the total weight of solid phase was 1.5 g. Furthermore, at the preparation of CSH gel, the substance of iodide ions in each sample was adjusted to 15 μmol. The synthesis procedure for all samples was conducted in a glove bag filled with nitrogen gas. The curing period was 7, 14, 30, and 60 days at a room temperature (298 K) with shaking at 120 strokes/min. The results of the sorption experiments, iodide ions adsorbed on CSH gel regardless of the high concentration of NaCl. The concentration of iodide ions in liquid phase was equal to the initial one under all experimental conditions. Moreover, the distribution coefficients, K_d, were kept constant (K_d = 1 mL/g) after 14 days. In the results of Raman analysis, the structure of CSH gel was scarcely influenced by incorporating iodide ions from the viewpoint of the silicate chain. These results suggest that iodide ions will be incorporated into CSH gel with the hydration water without changing its structure. Such effect of CSH gel formed with leaching cementitious constituents around the repository may retard the migration of radionuclide (I-129) in the natural barrier of the radioactive waste disposal system.

INTRODUCTION

In Japan, high-level radioactive wastes (HLW) and TRans-Uranium (TRU) radioactive wastes will be disposed by geological disposal. This facility requires an enormous amount of cementitious materials due to the construction in deep underground. After the backfilling of the repository, by contacting groundwater with cementitious materials for a long time, calcium (Ca), potassium (K) and sodium (Na) ions will leach into groundwater from the pores of the materials, and the pH of groundwater around the repository may change up to 13. Under such a condition, calcium silicate hydrate (CSH gel) with the wide range of Ca/Si molar ratio is

formed on the surface of flow-path as a secondary mineral by the reaction of Ca ions and silicate species dissolved from host rock. For assessing the performance of the natural barrier system for the repository, the interaction of radionuclides with CSH gel is one of the important factors because the sorption effect of CSH gel will retard the migration of radionuclides. In particular, I-129 contained in TRU wastes is a long half-life nuclide and easily migrates in underground [1]. Generally, anion nuclides hardly sorb to the host rock such as granite. However, the authors' previous study reported that CSH gel incorporates iodide ions with its formation though the dominant factors for such sorption behavior were not clear [2]. This present study focused on the influence of liquid/solid (L/S) ratio on the sorption behavior of iodide ions on CSH gel because the uptake of water with the formation of CSH gel may affect the sorption of anions. So far, in some previous studies, the interaction between radionuclides and CSH gel has been examined by using some dried CSH gel samples [3]. However, the underground environment including the repository is filled with groundwater after the closure. Therefore, this study applied CSH gel without drying process for the sorption experiments.

EXPERIMENTAL METHODS

The sorption experiments using CSH gel followed the basic procedures reported in our previous researches [2, 4-7]. Table 1 shows the parameters of the sorption experiments in this study. In the experiments, CSH gel was synthesized by mixing CaO (Wako Pure Chemical Industries Ltd.) and SiO_2 as fumed silica (AEROSIL 300 purchased from Japan AEROSIL LTD.) with NaCl solution in the glove bag filled with nitrogen gas. Ca/Si molar ratios of CSH gel were set to 0.4, 0.8, 1.2 and 1.6. With the preparation of CSH gel, 30 µL of 0.5 M NaI solution was added to each sample so as to adjust the substance of iodide ions to 15 µmol. The concentration of NaCl solution was set to 0.6 M for simulating the condition of saline groundwater. The total weight of CaO and SiO_2 in the solid sample was 1.5 g, and the total volume of liquid phase was 15, 19.5, 22.5, 25.5 or 30 mL. In other words, liquid/solid (L/S) weight ratios of the samples were set to 10, 13, 15, 17 or 20 mL/g respectively. The liquid volume in these conditions of L/S ratio was enough for the hydration of CSH gel. The curing period was 7, 14, 30 and 60 days at a room temperature (298 K) with shaking mechanically at 120 strokes/min.

Concerning L/S, general groundwater flow-paths including secondary minerals undergoes L/S remarkably smaller than 10. However, in order to measure the concentrations of ions and pH, a given volume of liquid phase is required. Such experimental limit constrains the lower bound of L/S. Therefore, this study selected L/S, as an experimental parameter, to examine the effects of L/S on the interaction of iodide ions with CSH.

Table 1 Materials used to synthesize CSH.

Liquid/Solid weight ratio	Ca/Si molar ratio	CaO (g)	SiO$_2$ (g)	Total weight of solid phase (g)	NaCl solution (mL)	NaI solution (μL)	Total volume of liquid phase (mL)
20	0.4	1.09	0.41	1.5	29.97	30	30
	0.8	0.86	0.64				
	1.2	0.71	0.79				
	1.6	0.60	0.90				
17	0.4	1.09	0.41		25.47		25.5
	0.8	0.86	0.64				
	1.2	0.71	0.79				
	1.6	0.60	0.90				
15	0.4	1.09	0.41		22.47		22.5
	0.8	0.86	0.64				
	1.2	0.71	0.79				
	1.6	0.60	0.90				
13	0.4	1.09	0.41		19.47		19.5
	0.8	0.86	0.64				
	1.2	0.71	0.79				
	1.6	0.60	0.90				
10	0.4	1.09	0.41		14.97		15
	0.8	0.86	0.64				
	1.2	0.71	0.79				
	1.6	0.60	0.90				

Table 2 The weight of solid phase and the volume of liquid phase after.

Liquid/Solid weight ratio	Ca/Si molar ratio	The weight of solid phase (g)	The volume of liquid phase (mL)
20	0.4	17.07	12.89
	0.8	15.01	15.54
	1.2	15.31	16.62
	1.6	12.69	16.94
17	0.4	14.73	9.44
	0.8	13.55	10.89
	1.2	12.82	11.91
	1.6	10.98	13.74
15	0.4	14.28	7.76
	0.8	12.87	7.92
	1.2	12.37	9.02
	1.6	10.8	11.81
13	0.4	14.58	4.29
	0.8	12.28	5.64
	1.2	11.35	8.37
	1.6	12.56	7.19
10	0.4	16.98	0
	0.8	14.51	0
	1.2	12.36	1.46
	1.6	12.37	5.78

After curing, each sample was centrifuged at 7500 rpm for 10 minutes. The supernatant solution pf each sample was filtered by 0.20 µm membrane filter. After the separation procedure, for the liquid phase, pH was monitored and the concentrations of iodide ions, Ca ions and Si ions were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (SPS7800, Seiko Instruments Inc.), respectively.

From the concentrations of Ca and Si, this study confirmed that Ca/Si ratio of solid phase (CSH gel) kept the given values in Table 1. In fact, the leaching amounts of Ca and Si were much smaller than the contents in CSH gel. Besides, the solid phase was measured Raman spectrum by laser Raman spectrophotometer (NRS-3300QSE, JASCO) used a YAG laser (532 nm) as an excitation lase in order to analyze the polymerization degree of the silicate chain in CSH gel. Many studies have reported that the structure of CSH gel is similar to tobermorite, which structure consists of hydrated Ca-O interlayer with the hydration water sandwiched between silicate chains [8].The polymerization degree of the silicate chain in the CSH gel is expressed as Q^n, where "n" shows the number of the bridging oxygen atoms (siloxane bond, Si-O-Si) [3, 9]. This study measured two peaks of symmetric stretching vibration, Q^1 (870 cm^{-1}) and Q^2 (1010 cm^{-1}). As in other researches, the peak intensity ratio of Q^1 and Q^2 in Raman spectra, i.s., Q^1/Q^2 was evaluated as an index showing the degree of polymerization of silicate chain in CSH gel. For example, a lower Q^1/Q^2 ratio means a higher degree of polymerization of silicate chain.

RESULTS AND DISCUSSION

Sorption of iodide ions on CSH gel

Fig. 1 shows the sorption of iodide ions on CSH gel after the curing of samples. The amount of iodide ions for the vertical axis was calculated from the concentration of iodide ions and the volume of liquid phase. Note that the volume of liquid phase decreases in comparison with the initial condition due to the hydration of CSH gel. For L/S=10 in Fig. 1, the data for Cs/Si=0.4, 0.8 and 1.2 are not shown because the volume of liquid phase after the curing time was not enough for the measurement of iodide ions. As shown in Fig. 1, iodide ions were significantly adsorbed on CSH gel under the all conditions. Furthermore, the lower the Ca/Si ratio of CSH gel was, the larger the sorption amount of iodide ions was. However, it may be difficult to discuss the sorption behavior by comparing the amount of iodide ions in liquid phase. As shown in Table 1, the volume of liquid phase and the weight of solid phase after curing are different according to the each condition of the Ca/Si ratio and the L/S ratio.
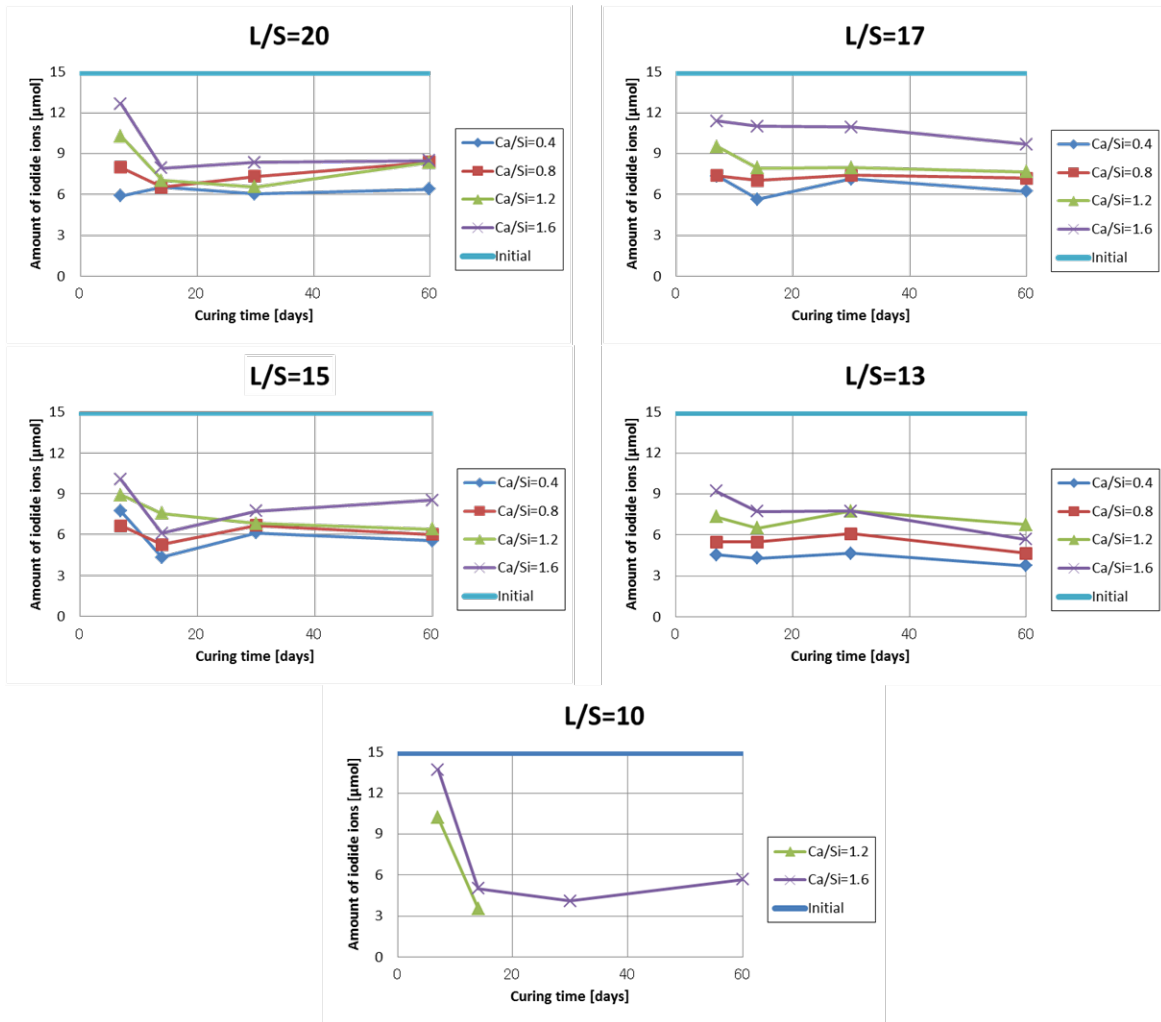
Fig. 1 Sorption of iodide ions into CSH gel.

Thus, considering such differences, the sorption distribution coefficient, K_d [mL/g], was calculated by

$$K_d \; [\text{ml/g}] = \frac{\dfrac{\text{Amount of iodide ions in the solid phase [mol]}}{\text{Weight of the solid phase [g]}}}{\dfrac{\text{Amount of iodide ions in the liquid phase [mol]}}{\text{Volume of the liquid phase [mL]}}} \; .$$

Fig. 2 shows that the time-dependencies of K_d. As shown in Fig. 2, the distribution coefficients kept constant at K_d = 1 ml/g after 14 days in curing time. That is to say, the CSH gel needs 14 days or at least more than 7 days to incorporate iodide ions and reach a stable condition.
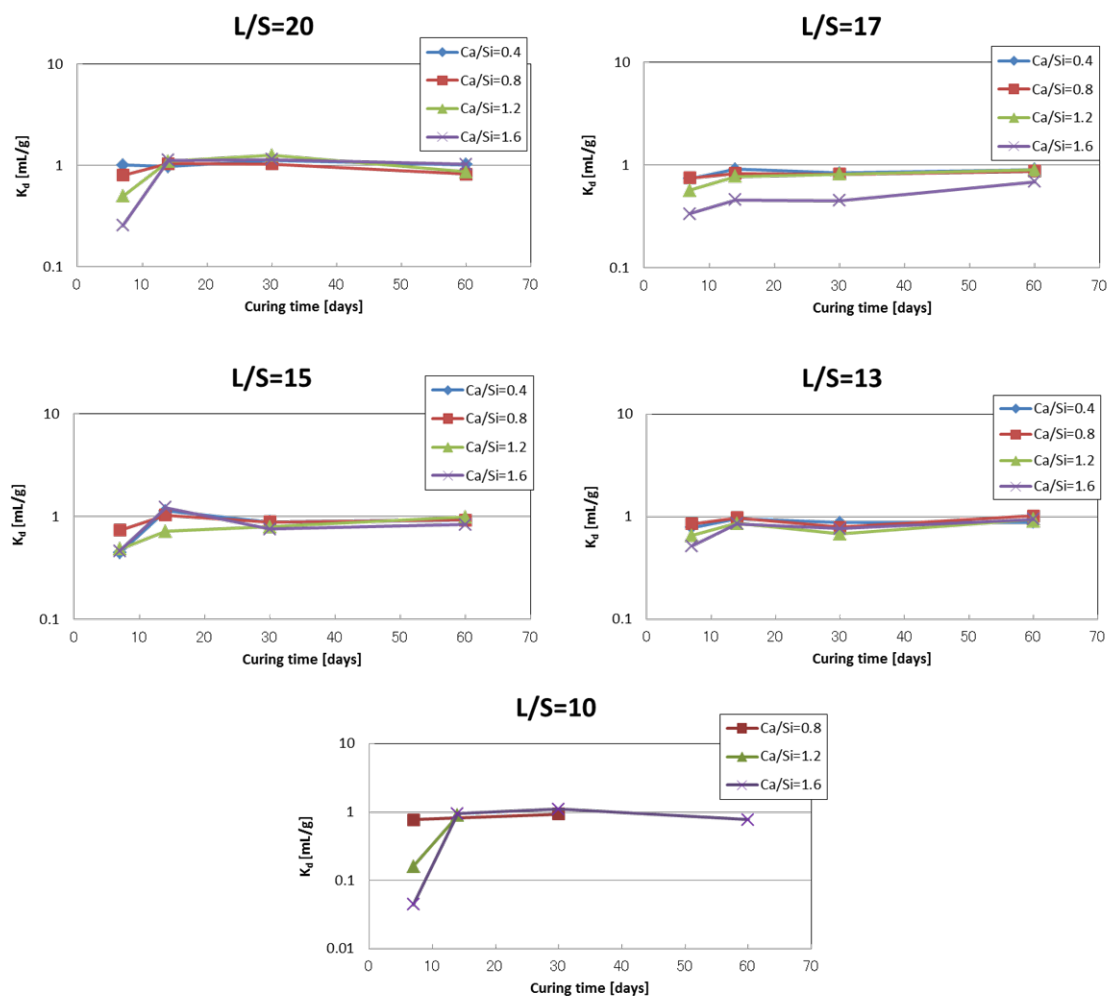
Fig. 2 Sorption distribution coefficient.

In addition, Fig. 3 shows the concentration of iodide ions in the liquid phase through the sorption experiments. The concentration of iodide ions in the liquid phase is almost equal to the initial concentration (blue lines in Fig. 3) after 14 days. Furthermore, as a remarkable points in these results, iodide ions sorbed into CSH gel in spite of the high concentration of chloride ions (0.6 M). Chloride ions, which are a monovalent anion at the same as iodide ions, would inhibit the sorption of iodide ions if the sorption behavior is based on the electrostatic process and the ion exchange. While the detail of the influence of chloride ions on the sorption behavior of iodide ions should be examined as a future work, these may suggest that the CSH gel incorporates iodide ions into its structure with the hydration water (chloride ions as well).
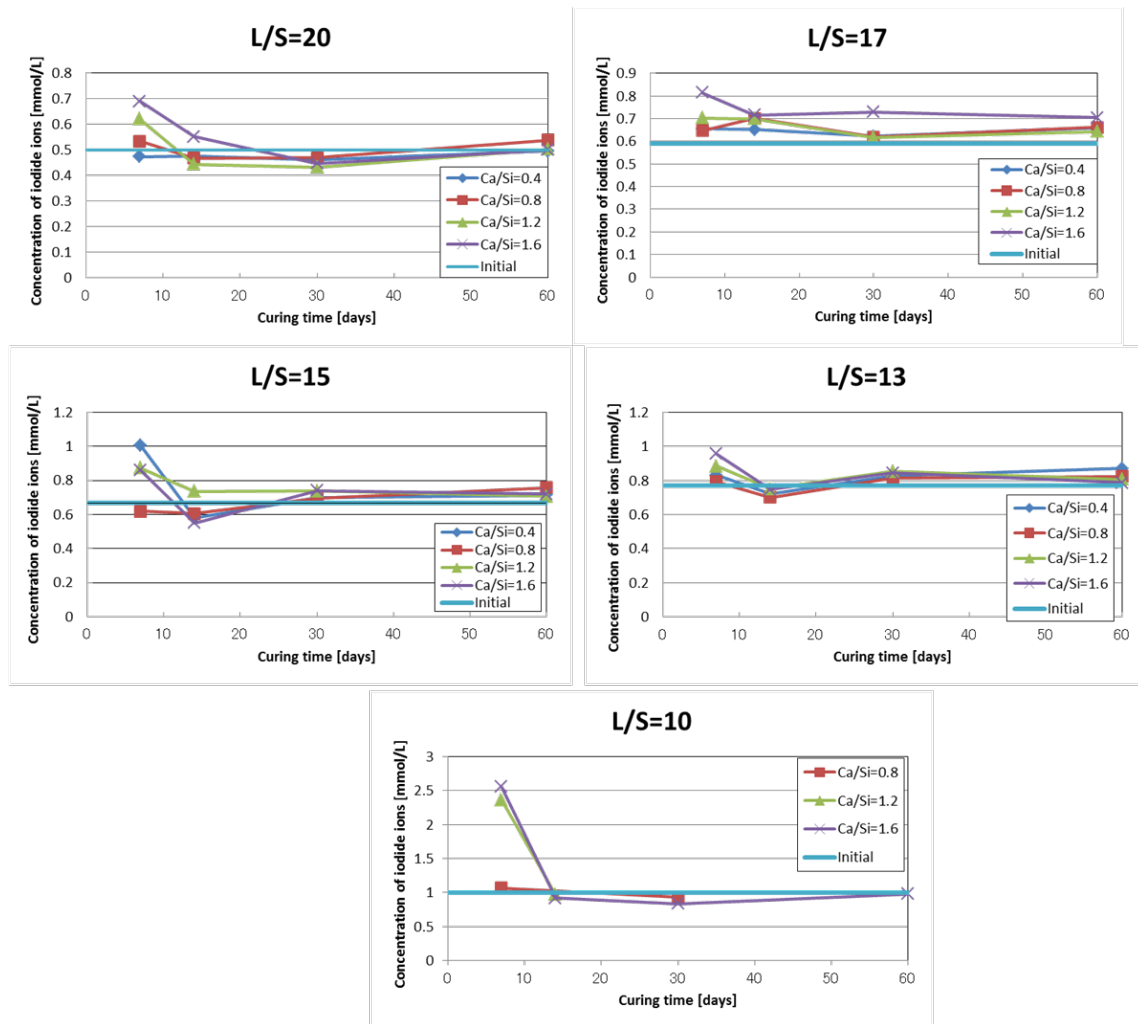
Fig. 3 Concentration of iodide ions in the liquid phase.

Change in the structure of CSH gel based on Raman analysis

Fig. 4 shows the Q^1/Q^2 ratios of CSH gel after the sorption experiments. The Q^1/Q^2 ratios for the samples of the lower Ca/Si molar ratio (Ca/Si = 0.4, 0.8) could not be estimated because the peak of Q^1 for these samples was not detected. Furthermore, the Q^1/Q^2 ratios for Ca/Si=1.2 were smaller than those for Ca/Si=1.6 as shown in Fig. 4. These mean the high polymerization-degree of silicate chain under the condition of the lower Ca/Si ratio. About the change with the curing time, the Q^1/Q^2 ratios did not change or became lower a little. This suggests that the polymerization of the silicate chain in CSH gel rapidly progresses at the formation of CSH gel.

Fig.5 shows the influence of iodide ions on the Q^1/Q^2 ratio. The Q^1/Q^2 ratio of samples does not almost change with iodide ions. In addition, the Q^1/Q^2 ratio hardly depends on the L/S ratio and the addition of iodide ions. These mean that the

structure of CSH gel forms identically regardless of the L/S ratio and the sorption of iodide ions when there is enough water for the hydration.
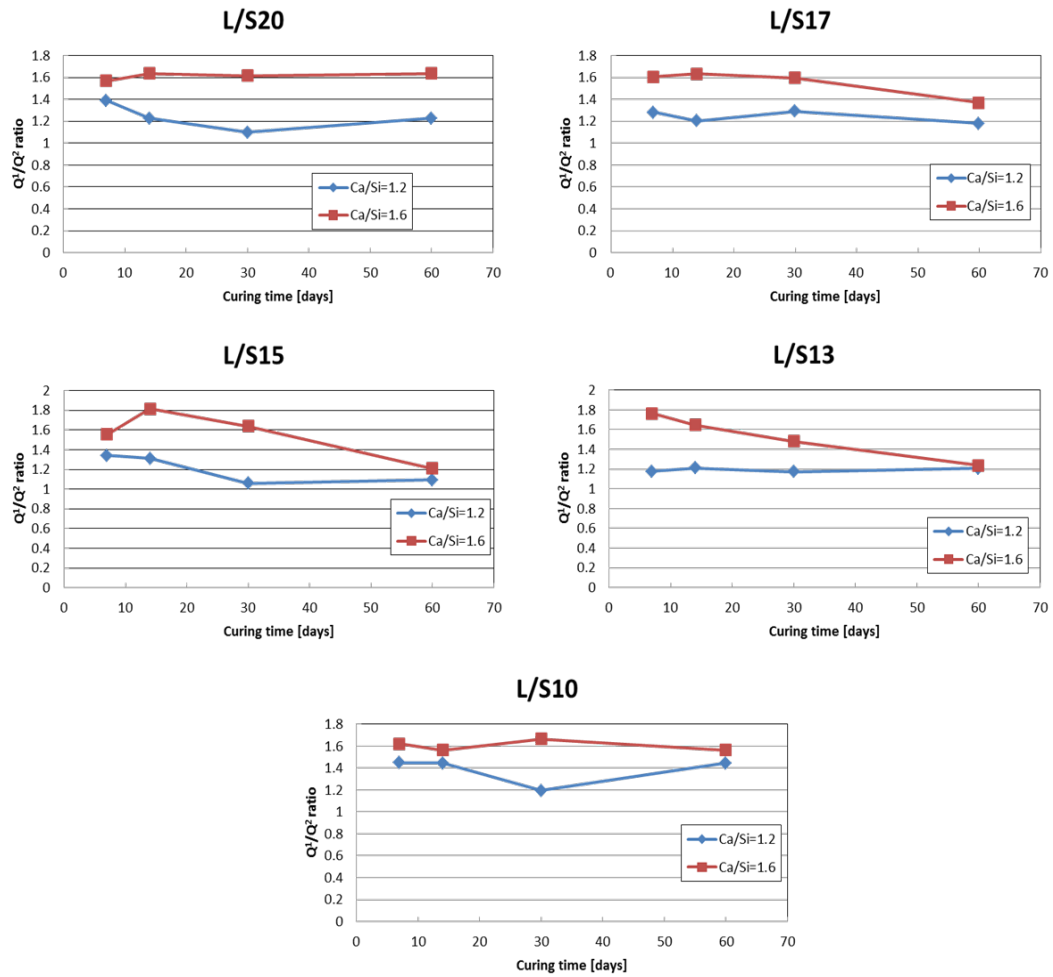
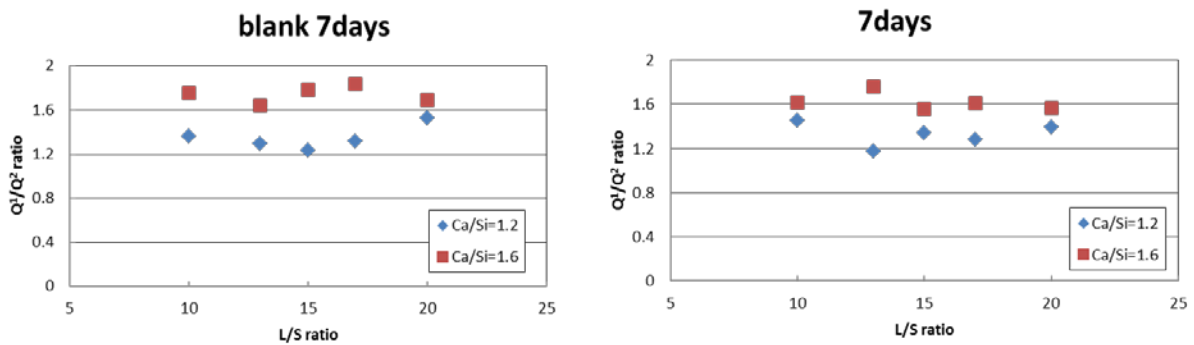Fig. 4 Q^1/Q^2 ratio of CSH gel after the sorption experiments.

Fig. 5 The comparison of Q^1/Q^2 ratio of the CSH gel by iodide ions or not.

Presently, the value of the sorption distribution coefficient of iodide ions for the host rock is used K_d = 0.1 ml/g in the performance evaluation of the disposal repository [9]. However, the value of the sorption distribution coefficient in this study was about 1 ml/g under a condition saturated by saline water (without drying process), and this exceeds the conventional setting value. Furthermore, the formation of CSH as a secondary mineral decreases porosity in the groundwater flow-paths. Therefore, such a formed CSH gel might retard the iodide ions in the near field of the repository.

Conclusions

This study discussed the sorption behavior of iodide ions on CSH gel formed under the condition saturated with saline water. The results of the sorption experiments, the amount of iodide ions in the liquid phase decreased in all samples. Such a sorption behavior became steady after 14 days of the curing time. On the other hand, the concentration of iodide ions in the filtered supernatant solution was equal to the initial ones under all experimental conditions in this study. Moreover, the distribution coefficients for the sorption of iodide ions on CSH gel were almost estimated as 1mL/g after 14 days of the curing time. In addition, the structure of CSH gel hardly changed regardless of the coexistence of iodide ions from the view point of the silicate chain. These experimental results suggest that CSH gel takes in iodide ions with the hydration water without changing its structure. That is, CSH gel formed as a secondary mineral around the repository will contribute to the immobilization of I-129.

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