

Sorption Behavior of Eu(III) into CSH Gel in Imitated Saline Groundwater - 12145

Taihei Funabashi*, Yuichi Niibori*, and Hitoshi Mimura*

* Dept. of Quantum Science & Energy Engineering, Graduate School of Engineering,
Tohoku University, 6-6-01-2, Aramaki, Aza-Aoba, Aoba-ku, Sendai, 980-8579 JAPAN

ABSTRACT

The sorption behavior of Eu(III) (europium (III)) into CSH (Calcium Silicate Hydrate) gel without dried processes was examined in imitated saline groundwater by using the spectrofluorometer, Raman spectrophotometer and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry). Ca/Si ratio was set to 0.4, 0.8, 1.2 and 1.6, and NaCl concentration was also set to 0.6, 0.06 and 0.006. The synthesis of each sample was conducted in a glove box saturated with nitrogen gas. The sealed sample tubes were gently shaken with 120 strokes/min. The time-period to contact Eu(III) with the CSH gel was set to 60 days.

The fluorescence emission spectra suggested the incorporation of Eu^{3+} into CSH gel in the high Ca/Si ratio samples. On the other hand, from the decay behavior of fluorescence emission spectra, even in the low Ca/Si ratio samples, sorption behavior of Eu^{3+} into CSH gel was confirmed. Besides, the Raman spectra showed that the degree of polymerization of Si-O in CSH gel was raised with increasing Na ions concentration. These results suggest that the CSH gel, formed as secondary mineral, would retard the migration of radionuclides even in saline groundwater.

INTRODUCTION

Since the Japanese repository system of high level radioactive wastes is constructed under the water table, a large amount of cementitious material is required for avoiding inflow of groundwater to the repository during the construction, the operation and the monitoring periods. After the backfill of such a deep geological repository, the contact of groundwater with cementitious materials leads the high alkalization of groundwater containing rich Ca ion [1,2]. On the other hand, a large amount of silica exists around the repository, and the solubility of silica increases at high pH [3]. These suggest that the CSH gel (with relatively low Ca/Si ratio < 1.0) as a secondary mineral is precipitated around the repository saturated with groundwater. Narita et al. [4] prepared the CSH gel (Ca/Si ratio=0.1 through 1.8), and examined the sorption of Eu^{3+} into CSH gel without the process of drying. Here, Eu^{3+} was used as an alternative element of Am^{3+} . The results showed the strong sorption of Eu^{3+} into the CSH gel even with relatively low Ca/Si ratio. While these experiments were carried out in Na-free solution, the inflow of saline groundwater into repository site must be also considered particularly in Japan [1]. So far, some researches have examined such an effect of Na ions on the sorption behavior of radionuclides [e.g., 5]. However, its behavior to CSH gel of relatively low Ca/Si ratio without dry process has not been sufficiently discussed.

Considering a condition saturated again with groundwater after the backfill, this study examined the effect of NaCl on the interaction of radionuclides and CSH gel (0.4, 0.8, 1.2 and 1.6 in Ca/Si mol ratio) with no dry processes. By using the fluorescence spectra, the Raman spectra and some ion concentrations, this study discusses whether that CSH gel (formed as a secondary mineral

around the repository) also can retard the migration of radionuclides even if the repository and its surrounding are saturated by saline groundwater.

EXPERIMENTAL

Samples

In the same way as previous studies [4,6,7], in this study three types of CSH samples were prepared: (1) 1 mM $\text{Eu}(\text{NO}_3)_3$ in 1 mM HNO_3 is added after curing CSH gel (surface sorption sample). (2) 1 mM $\text{Eu}(\text{NO}_3)_3$ in 1 mM HNO_3 is added before curing CSH gel (co-precipitation sample). (3) CSH gel was prepared without adding Eu^{3+} (Eu-free sample). Eu^{3+} was used as an alternative element of Am^{3+} . Ca/Si ratio of samples was set to 0.4, 0.8, 1.2 and 1.6. In addition, NaCl solution was used as an imitated saline groundwater. NaCl concentration of samples was set to 0.6, 0.06 and 0.006. Each sample was synthesized with CaO, SiO_2 , and distilled saline water in a given combination as shown in Table I. SiO_2 (Fumed Silica, AEROSIL 300) was obtained from Japan AEROSIL Ltd. The specific surface area of BET (N_2 gas) was $300 \pm 30 \text{ m}^2/\text{g}$. The other chemicals were obtained from Wako Pure Chemical Industries Ltd.

Table I. Materials Used to Synthesize Sample.

Ca/Si ratio	CaO /g	SiO_2 /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

Procedure

The study followed the basic experimental procedures already reported by the authors [4,6,7]. In order to avoid contact with air, the synthesis of each sample was conducted in the glove bag saturated with Nitrogen gas. “Surface sorption sample” was cured for 7 days in the sample tubes, sealed and constantly shaken with 120 strokes/min before contacting with $\text{Eu}(\text{NO}_3)_3$ solution. The curing period of CSH gel was determined by both concentrations of Ca and Si in the solution reached equilibrium. The contacting time-period of Eu and CSH gel was set to 60 days. Through the same way as the procedure of curing CSH gel, the sealed sample tube including Eu and CSH gel was shaken. The temperature was kept constant within $298 \pm 0.5 \text{ K}$. On the other hand, “co-precipitation sample” was already included 1 mM $\text{Eu}(\text{NO}_3)_3$ in the synthesis process of CSH gel. In this sample also, the contacting time-period of Eu and CSH gel was set to 60 days. The shaking rate and the temperature were similarly fixed to those for the surface sorption samples. “Eu-free sample” was prepared except adding Eu ions in the same way as the co-precipitation sample. All samples were adjusted without the drying process. After the above procedures, this study obtained both the fluorescence emission spectra and the fluorescence lifetime from the surface sorption sample and the co-precipitation sample. Fluorescence emission spectra was measured by spectrofluorometer (JASCO, FP-6500), where 390 nm xenon lamp was used for exciting Eu^{3+} in the solution. In addition, decay behavior of

fluorescence emission spectra were measured by spectrofluorometer (HORIBA JOBIN YVON, FluoroCube 3000U). Here, Eu in sample solution was excited by 390 nm LED (Light Emitting Diode). The decay behavior of emission wavelength was examined at 592 nm. Furthermore, the samples were separated into liquid and solid phase by centrifuge. The liquid phase was filtrated by 0.20 μm membrane filter. Then, the concentrations of Ca, Eu, Si and Na were measured by ICP-AES. Besides, the Raman spectra were obtained from the solid phases of the surface sorption sample, the co-precipitation sample and Eu-free sample. The Raman spectra were measured by laser Raman spectrophotometer (JASCO, NRS-3300), where 532 nm YAG (Yttrium Aluminium Garnet) laser was used for Raman scattering.

RESULT AND DISCUSSION

Fluorescence Emission Spectra and Fluorescence Lifetime

Figure 1 shows the fluorescence emission spectra of surface sorption samples and co-precipitation samples. The change of spectra due to difference of NaCl concentration was not observed in these samples. On the other hand, Ca/Si ratio remarkably affected the spectra. The previous reports [4,6,7] have explained that the split of peak at 618 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition) means the incorporated of Eu^{3+} into CSH gel. Therefore, it is considered that, even in saline groundwater system, the samples of Ca/Si ratio >0.8 incorporate Eu^{3+} into the inside of CSH gel.

Figure 2 shows the decay behavior of fluorescence emission spectra of surface sorption samples and co-precipitation samples. Here, "filtrate" in this figure means a solution filtrated from the liquid phase of CSH gel (Ca/Si ratio: 1.0, the curing time: 7 days) by 0.20 μm membrane filter. Its filtrated solution (pH 11.8) was contacted with 1 mM $\text{Eu}(\text{NO}_3)_3$ solution. In the filtrated solution, Eu^{3+} mainly exists as $\text{Eu}(\text{OH})_3$ colloid. Such a fluorescent intensity decreases exponentially with time [4]. However, the decay behavior of fluorescence in the presence of CSH gel showed a curve in the logarithm of the intensity, as shown in Figure 2. This suggests that Eu^{3+} has various hydrated structures to interact with CSH gel. In addition, fluorescence lifetime was evaluated. So far, a fluorescence lifetime has been defined as the time when the intensity of fluorescence decreases to the e^{-1} time. Therefore, the fluorescence lifetime cannot be strictly defined from the intensity except for exponentially-decaying [8]. This study evaluated fluorescence lifetime in the co-presence of CSH gel from a slope in the range from 1.0 ms to 2.0 ms as an indicator.

Table II indicates the fluorescence lifetime. Each sample undergoes longer fluorescence lifetime than that of the "filtrate" sample. The fluorescence lifetime of $\text{Eu}(\text{OH})_3$ is short due to OH oscillators included in the inner coordination sphere of Eu(III) ion. In other words, the fluorescence lifetime longer than that of the filtrate sample shows Eu^{3+} interacted with the solid phase. Therefore, even in the samples of Ca/Si ratio 0.4, Eu^{3+} is not only hydrolyzed to form $\text{Eu}(\text{OH})_3$ colloid, but is also forming complex on the surface of solid phase. In addition, NaOH concentration does not apparently affect the fluorescence lifetimes of surface sorption samples and co-precipitation samples. This is harmonic to the effects of Na ions predicted through the fluorescence emission spectra mentioned above.

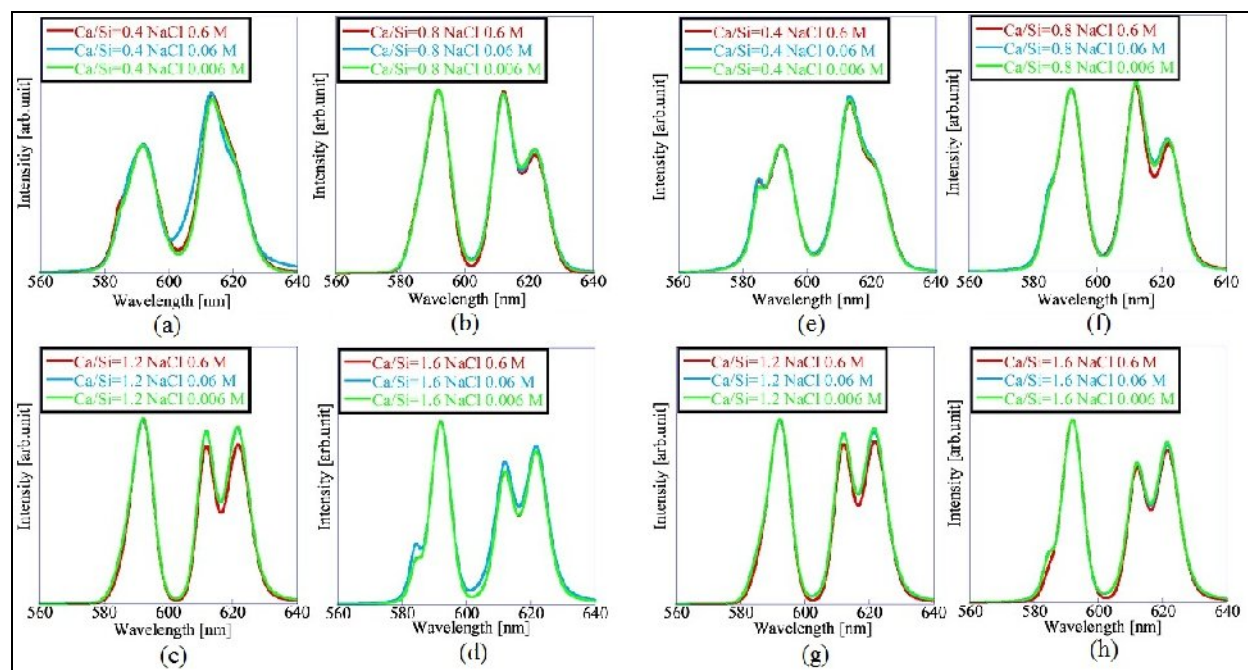


Fig. 1. Fluorescence emission spectra ((a) through (d) = “Surface sorption sample”, and (e) through (h) = “Co-precipitation sample”.)

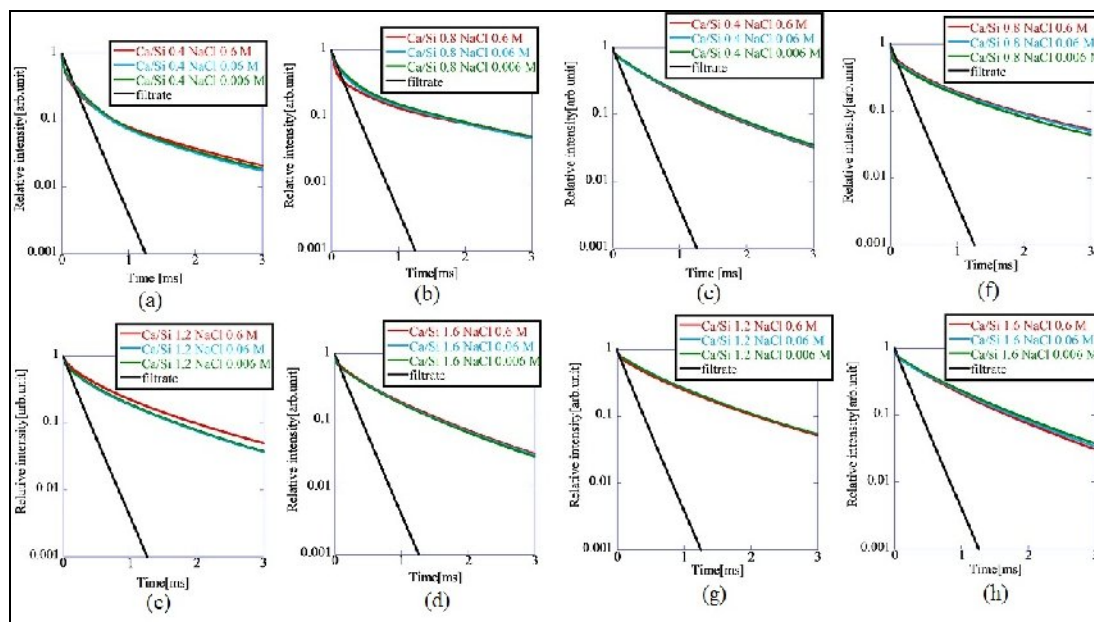


Fig. 2. Delay behavior of fluorescence emission spectra ((a) through (d) = “Surface sorption sample”, and (e) through (h) = “Co-precipitation sample”).

Table II. Fluorescence Lifetime of Each Sample and Filtrate.

Fluorescence lifetime (ms)						
	Concentration of NaCl (M)	Ca/Si ratio				filtrate
		0.4	0.8	1.2	1.6	
surface sorption	0.006	1	1.288	1.152	1.033	0.11
	0.06	0.983	1.364	1.144	1.011	
	0.6	0.984	1.367	1.179	0.975	
co-precipitation	0.006	1.246	1.615	1.119	1.008	
	0.06	1.234	1.612	1.118	1.032	
	0.6	1.351	1.857	1.210	1.035	

Concentrations of Eu, Ca, Si, and Na in Solution.

Eu(III) was detected in neither solution sample filtrated through 0.2 μm membrane filter from the surface sorption samples or the co-precipitation samples. Hereinafter, this study indicates the concentrations of Ca, Si and Na in the solution to discuss the incorporation of Eu(III) into CSH gel obtained without dry processes.

Tables III, IV and V show the concentration of Ca Si, and Na of each samples in liquid phase after the reaction time-period (60 days). Especially in the sample of low Ca/Si ratio, Ca concentration was raised with increasing the initial concentration of Na ions. This means a tendency of ion-exchange of Ca (in CSH gel) and Na in the solution. Furthermore, the decrease of Si concentration in low Ca/Si ratio sample was observed with increasing the initial concentration of Na ions, while in the samples of Ca/Si ratio 1.6 the Si concentration slightly increased. These tendencies were observed in the "surface sorption samples", "co-precipitated samples" and "Eu-free samples".

Figure 3 shows the Ca/Si ratios of solid phase after 60 days, compared to the initial ratio of the synthesized CSH samples. Here, the Ca/Si ratios of solid phase after 60 days were calculated by using the amounts both of Ca and Si used to synthesize sample (Table I) and the ion concentrations indicated in Table III, IV and V. As shown in Figure 3, the Ca/Si ratios in the solid phase were mostly maintained at the initial values within the experiment time-period, while some ion-exchange of Ca and Na was observed as shown in Table III, IV, and V. However, in the sample of relatively high Ca/Si ratio, the Ca/Si ratio after 60 days tends to become slightly lower than the initial value. Sugiyama et al. [5] reported that Na ions increase the solubility of Ca and Si in the co-presence of CSH gel. It is confirmed that such a tendency appeared even in the CSH sample of relatively high Ca/Si ratio synthesized without dry processes.

Table III. Concentration of Ca, Si and Na of Surface Sorption Samples.

	Ca/Si ratio	initial Na [M]	solid phase		
			Ca [mM]	Si [mM]	Na [mM]
surface sorption	0.4	0.006	4.938	3.013	3.247
		0.06	10.526	2.747	41.847
		0.6	24.146	2.171	473.203
	0.8	0.006	4.689	0.434	3.497
		0.06	10.478	0.364	40.638
		0.6	27.561	0.285	472.020
	1.2	0.006	15.448	0.065	5.543
		0.06	17.592	0.056	50.136
		0.6	25.173	0.064	485.098
	1.6	0.006	28.010	0.025	5.817
		0.06	27.709	0.041	53.032
		0.6	32.070	0.038	515.385

Table IV. Concentration of Ca, Si and Na of Co-precipitation Samples.

	Ca/Si ratio	initial Na [M]	solid phase		
			Ca [mM]	Si [mM]	Na [mM]
co-precipitation	0.4	0.006	4.484	3.050	3.259
		0.06	9.405	2.673	39.432
		0.6	21.848	2.133	444.118
	0.8	0.006	4.237	0.675	3.094
		0.06	10.797	0.531	39.847
		0.6	25.723	0.328	447.233
	1.2	0.006	12.862	0.054	5.251
		0.06	14.780	0.065	49.634
		0.6	24.563	0.044	485.940
	1.6	0.006	28.992	0.011	5.950
		0.06	27.625	0.011	50.038
		0.6	31.430	0.015	505.881

Table V. Concentration of Ca, Si and Na of Eu-free Samples.

	Ca/Si ratio	initial Na [M]	solid phase		
			Ca [mM]	Si [mM]	Na [mM]
Eu-free	0.4	0.006	2.711	3.259	3.076
		0.06	8.753	2.554	41.861
		0.6	22.672	2.035	489.137
	0.8	0.006	2.395	0.714	2.839
		0.06	8.884	0.452	39.090
		0.6	26.030	0.295	483.107
	1.2	0.006	12.925	0.055	5.544
		0.06	14.511	0.045	51.683
		0.6	23.776	0.040	517.087
	1.6	0.006	27.030	0.015	6.159
		0.06	25.865	0.016	54.583
		0.6	30.099	0.017	527.236

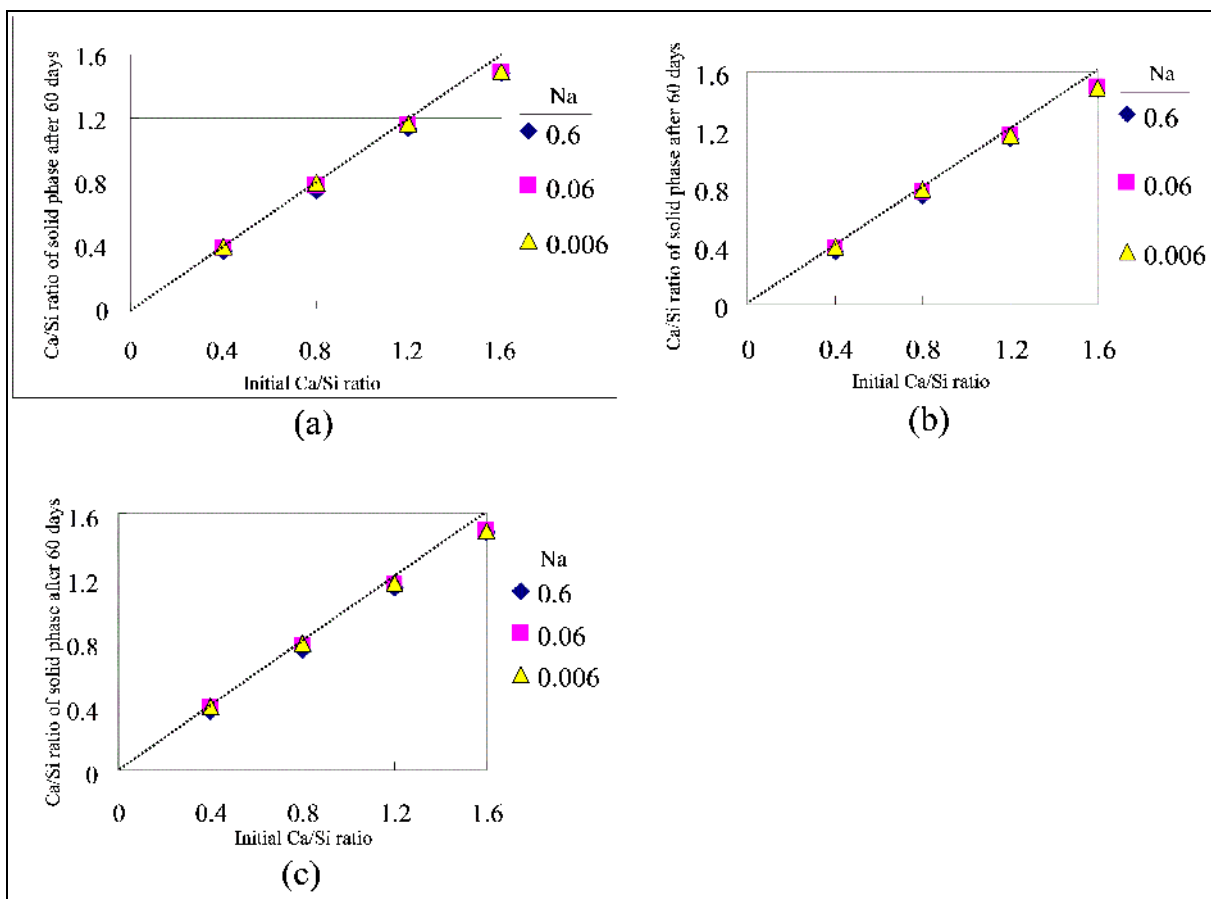


Fig. 3. Ca/Si ratio of the solid phase ((a): “Surface sorption sample”, (b): “Co-precipitation sample”, and (c): “Eu-free sample”).

Raman Spectra

From the concentrations of Eu, Ca, Na, and Si measured by using ICP-AES, in the low Ca/Si ratio sample, the changes of Ca and Na ions suggested the sorption of Na ions into the internal structure of CSH gel or on its surface. In this study, the influence of the sorption of Na ions on the structure of CSH gel was examined by Raman spectra. So far, many studies have investigated the structure of CSH gel, indicating that the structure of CSH gel is similar to tobermorite [9-12]. The primary structure of tobermorite consists of silicate chain and CaO layer (sheet), where silicate chain is located in the interatomic spacings of the Ca–O sheet. The polymerization degree of SiO₄ tetrahedrons in the silicate chains is described by Qⁿ units, where n is the number of bridging oxygen atoms [13,14]. In Raman spectra of SiO₄ tetrahedrons, this study especially focused on the peaks of symmetric stretching vibration of Q¹ (870 cm⁻¹) and Q² (1010 cm⁻¹).

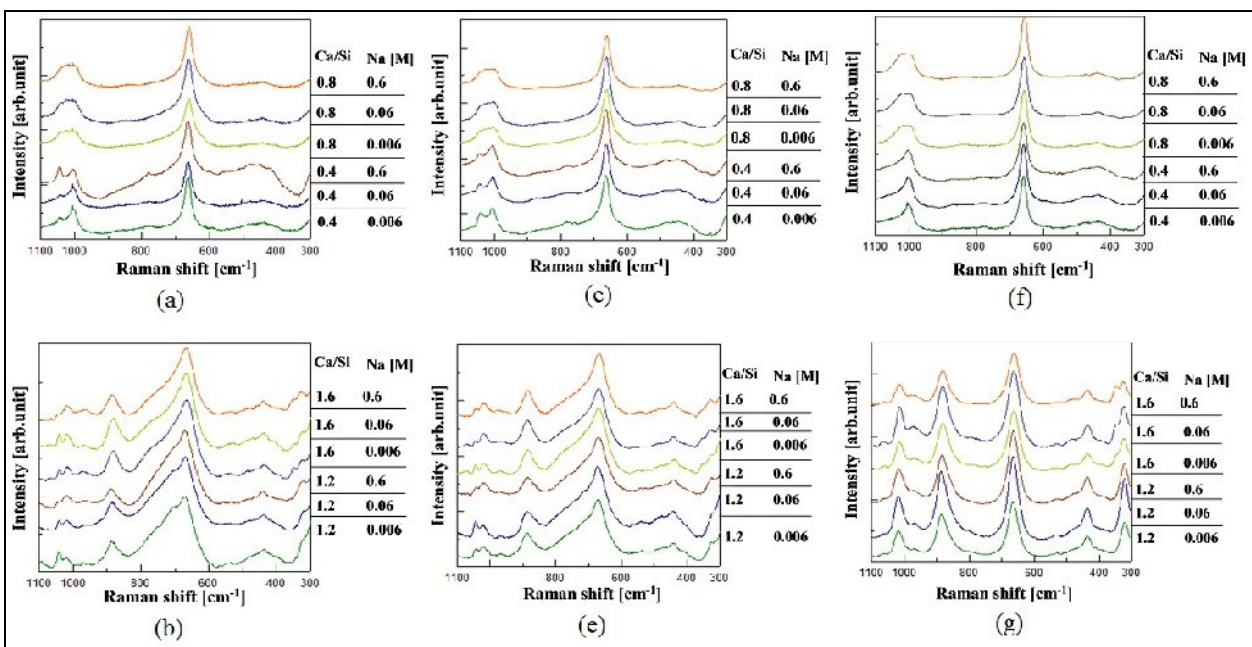


Fig. 4. Result of raman spectrum ((a) and (b) = “Surface sorption sample”, (c) and (d) = “Co-precipitation sample”, and (f) and (g) = “Eu-free sample”).

Figure 4 shows Raman spectra of each sample. In the low Ca/Si ratio samples (Ca/Si = 0.4 and 0.8), the peak of symmetric stretching vibration of Q¹ were not observed. On the other hand, in the high Ca/Si ratio samples (Ca/Si = 1.2 and 1.6), the peak of Q¹ were apparently confirmed. In general, it is well known that the higher Ca/Si ratio is, the stronger the intensity of Q¹ is [e.g., 12]. Table VI shows the intensity ratio of Q¹/Q². The intensity ratios of Q¹/Q² of surface sorption samples and co-precipitation sample became smaller with increasing initial Na concentration. This means that the degree of polymerization becomes larger in silicate chain of CSH gel. If Na ions electrostatically sorb on the solid surface, Na ions might not affect the macro structure of CSH gel. The decrement in the intensity ratio of Q¹/Q² suggests that CSH gel become stable with changing its structure in the co-presence of Na ions. Such a deforming of the macro structure of CSH gel may also affect the incorporation processes of Eu³⁺ into the CSH gel.

Table VI. Relation of Initial Na Concentration and Intensity Ratio of Q^1/Q^2 .

	Ca/Si ratio	initial Na [M]	Intensity ratio of Q^1/Q^2
surface sorption	1.2	0.006	2.154
		0.06	2.194
		0.6	1.407
	1.6	0.006	2.169
		0.06	2.064
		0.6	1.625
co-precipitation	1.2	0.006	1.872
		0.06	1.700
		0.6	1.327
	1.6	0.006	2.211
		0.06	2.016
		0.6	1.882
Eu-free	1.2	0.006	1.682
		0.06	1.720
		0.6	1.438
	1.6	0.006	1.717
		0.06	1.727
		0.6	1.738

CONCLUSIONS

Considering the inflow of saline groundwater into repository, this study examined the interaction between CSH gel (without dry processes) and Eu^{3+} by using the fluorescence emission spectra, the decay behavior of fluorescence and the Raman spectra. As a result, the fluorescence emission spectra of the sample of more than 0.8 Ca/Si ratio confirmed the intensity split into two peaks around 618 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition). Furthermore, even in relatively low Ca/Si ratio samples, the fluorescence lifetimes both of the surface sorption sample and the co-precipitated samples exceeded that of the filtrate sample. These suggested that Eu^{3+} is not only hydrolyzed to form $\text{Eu}(\text{OH})_3$ colloid, but is also stably incorporated into CSH gel (in Ca/Si ratio > 1.2) or is forming complex on the surface of solid phase (in Ca/Si < 0.8) in the co-presence of Na ions.

On the other hand, the concentrations of Na, Ca and Si after 60 days in the solution filtrated through 0.2 μm membrane filter showed the ion exchange of Ca and Eu apparently in the samples of low Ca/Si ratio. Besides, in the samples with high Ca/Si ratio, Ca and Si concentrations in the solution were raised with increment of initial Na concentration. While Na ions may slightly increase the solubility of CSH gel, the CSH samples were stable, mostly maintaining the initial Ca/Si ratio synthesized. Moreover, the Raman spectra showed that the degree of polymerization of silicate chain in CSH samples increased with increasing Na concentration. Such an immobilized Na into the structure of CSH gel did not obstruct the incorporation of Eu^{3+} into CSH gel.

The results mentioned above suggested that CSH gel (formed as a secondary mineral around the repository) also can retard the migration of radionuclides even if the repository and its surrounding are saturated by saline groundwater.

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