

Sorption Behavior of Eu(III) Into Calcium Silicate Hydrate (CSH) Gel With Relatively Low Ca/Si Ratio <1.0 – 10096

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ABSTRACT

A large amount of cement is needed to construct a geological disposal system in Japan. The main hydrate of cement paste is calcium silicate hydrate (CSH) gel, and it may alter the pH of groundwater to up to 13 around the repository. Since such highly alkaline groundwater (plume) contains rich Ca ions in addition to Na and K ions, in the dilution into the near field after the backfill, the Ca ions would react with soluble silicic acid, and deposit CSH gel again as a secondary mineral on the flow-path surface in the natural barrier. While a main concern is alteration of the multi-barrier system due to the high alkaline condition, the secondary minerals of CSH gel may also play a role in retarding the migration of radionuclides from the repository.

Generally, secondary CSH gel has a relatively low Ca/Si ratio, compared to original cement paste ($1.6 < \text{Ca/Si} < 1.8$) used for the construction. This study focused on the behavior of sorption of Eu(III) into CSH gel with a relatively low Ca/Si ratio ≤ 1.0 , using the fluorescence emission spectrum and its decay curve. Here, Eu(III) was used as a chemical analog of Am(III). For the observation of sorption behavior of Eu(III), this study prepared CSH samples with the Ca/Si ratio set to 1.8, 1.6, 1.0, 0.8, 0.5, 0.3 and 0.1. Each sample was synthesized with CaO, SiO₂, and distilled water in a given combination. A 1 mM Eu(III) solution is added after curing the CSH gel (hereinafter referred to as the “surface sorption sample”). This study also prepared the co-precipitated samples of CSH gel and Eu(III), where the 1 mM Eu(III) solution is added before curing the CSH gel. For all samples, the contact time-period of the CSH gels with Eu(III) was set to 30 days.

As for the surface sorption sample with a relatively high Ca/Si ratio ≥ 1.0 , its fluorescence emission spectrum at 618 nm was split into two peaks, as shown in the co-precipitated samples. This suggests that Eu(III) is incorporated by the CSH gel. On the other hand, the samples of the relatively low Ca/Si ratio < 0.8 showed a spectrum profile similar to that of a solution filtrated from the suspension of CSH gels. In the filtrate sample, Eu(III) is hydrolyzed to form Eu(OH)₃ colloid. However, the decay behaviors of the fluorescence emission spectrum were quite different between the filtrate samples and low Ca/Si ratio samples. That is, the low Ca/Si ratio

samples underwent slow attenuation of fluorescence and showed profiles similar to those of high Ca/Si ratio samples. This means that low Ca/Si ratio samples include the reaction forming a complex on the surface of CSH gel with Eu(III). In other words, such complex-forming reaction of secondary CSH gels would retard the migration of radionuclides.

INTRODUCTION

Cementitious material is used as constructional material or barrier material of the repository system of radioactive wastes [1]. Because of K^+ , Na^+ and Ca^{2+} in the pore water of cementitious material, groundwater around the repository may include high-alkali components [2]. On the other hand, SiO_2 exists voluminously around the geological disposal location. Since in a high pH range, the solubility of silicic acid (H_4SiO_4) becomes large, and high pH groundwater can dissolve SiO_2 . Moreover, the soluble silicic-acid, contacting the Ca ions, deposits as CSH gel on the surface of the flow-path [3]. For this reason, CSH gel (with a relatively low Ca/Si ratio ≤ 1.0) would be formed as a secondary mineral around the repository.

The sorption of radionuclide (RNs) onto CSH gel is controlled by the Ca^{2+} ion-exchange reaction. For example, Sr(II), Cs(I) and Ra(II) can take sorption forms, both on the surface of CSH gel and in the interlaminar of the SiO_2 chain [4,5]. Also, Cm(III) and Eu(III) can be ingested into the CSH gel surface sorption site and solid phase sorption site [6,7]. So far, dried samples of CSH gel have been used in order to examine the interaction of CSH gel with RNs. However, CSH gel formed around the repository (as secondary minerals with a relatively low Ca/Si ratio of 1.0) would be in the condition saturated with groundwater, because the Japanese repository (deeper than 300 m) would be constructed under the water table. Therefore, this study used CSH samples existing in aqueous solution (without dried processes) and examined the fluorescence emission spectra of Eu(III) in CSH gels. These results would suggest the effect of cementitious materials on the migration of RNs after backfilling the repository.

EXPERIMENTAL

Samples

For observing the sorption behavior of Eu(III), the two types of CSH samples were prepared by the following procedures: (1) 1 mM $Eu(NO_3)_3$ in 0.1 M HNO_3 is added after curing the CSH gel (hereinafter referred to as the “surface sorption sample”), (2) 1 mM $Eu(NO_3)_3$ in 0.1 M HNO_3 is added before curing the CSH gel (as the “co-precipitation sample”), where Eu(III) is included in the structure of CSH gel as the CSH gel is hydrated [7]. This study prepared CSH samples with the Ca/Si ratio set to 1.8, 1.6, 1.0, 0.8, 0.5, 0.3 and 0.1. Each sample was synthesized with CaO, SiO_2 , and distilled 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., and were used without further purification.



Fig.1. An example of CSH sample in this study (Ca/Si=1.0).

Table I. Materials used to synthesize CSH gel.

Ca/Si ratio	CaO / g	SiO ₂ / g	distilled water / ml
1.8	0.90	0.536	28.7
1.6	0.80	0.536	26.7
1.0	0.70	0.75	29.0
0.8	0.60	0.80	28.0
0.5	0.50	1.07	31.4
0.3	0.30	1.07	27.4
0.1	0.10	1.07	23.4

Procedures

Figure 2 shows the details of the experimental procedure including the synthesis of each sample. These main processes were based on the procedure already reported by the authors [8]. The synthesis of each CSH gel sample was conducted in a glove box saturated with nitrogen gas, in order to avoid contact with air. The temperature was kept constant within 298 ± 0.5 K. “The surface sorption sample” was cured for 7 days in the sample tubes, sealed, and gently shaken with 120 strokes / min before contacting with the Eu^{3+} solution. The curing time-period was determined so that both concentrations of Ca and Si reached equilibrium in the solution. The achievement of the equilibrium was confirmed by the X-ray diffraction pattern of solid phases. The concentrations of Ca and Si were measured by inductively-coupled plasma atomic emission spectrometry (ICP-AES). After 7 days for curing “the surface sorption sample”, Eu^{3+} solution was added into the tube containing “the surface sorption sample” of CSH gels. The contact time-period was set to 30 days. On the other hand, for the “co-precipitation sample” already containing 1 mM Eu^{3+} in the synthesis process of CSH gels, the curing time-period was set to 30 days. The concentration of Eu was also measured by ICP-AES. After each contact time-period, a 3 ml aliquot of the solution was pipetted out and its fluorescence emission spectrum and the decay behavior of the fluorescence emission spectrum were measured.

Fluorescence emission spectrum of Eu(III) was measured by spectrofluorometer (JASCO, FP-6500). In order to excite Eu(III) in sample solutions, 390 nm xenon lamp was irradiated. In addition, decay behavior of the fluorescence emission spectrum was measured by spectrofluorometer (HORIBA JOBIN YVON, FluoroCube 3000U). Eu(III) in sample solutions was excited by 390 nm LED and measured decay behavior of emission wavelength at 592 nm.

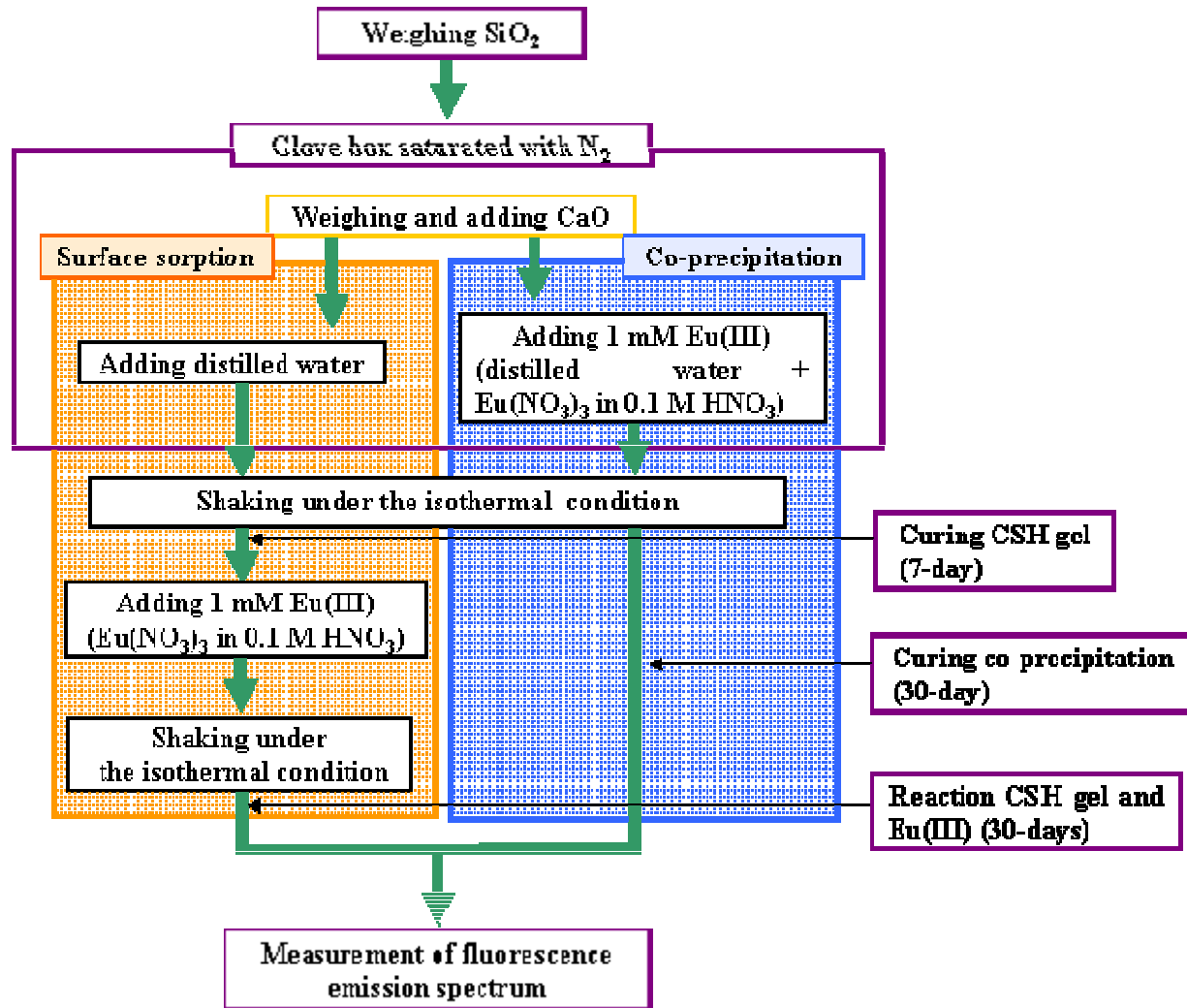


Fig.2. Procedure of the experiment.

RESULTS AND DISCUSSION

Figure 3 shows the fluorescence emission spectra in the absence of CSH gel. Here, the “Filtrate” means a solution filtrated from the suspension of CSH gels (cured for 7 days) by 0.20 μm membrane filters. Its filtrated solution (pH 11.8) was contacted with a 1 mM Eu(III) solution. On

the other hand, “NaOH” is a NaOH solution containing only 1 mM Eu(III). The concentration of NaOH was adjusted so that its pH became equal to that of the “Filtrate”. Under the condition of a high pH, nearly all Eu(III) exists as $\text{Eu}(\text{OH})_3$ colloid. As shown in Fig. 3, the fluorescence emission spectrum of the “NaOH” solution is similar to that of the “Filtrate”. This suggests that Eu is hydrolyzed to form $\text{Eu}(\text{OH})_3$ colloid also in the “Filtrate”.

Next, the fluorescence emission spectra of Eu(III) in the presence of CSH gels were measured. Figure 4 shows the spectra of the surface sorption sample, and Figure 5 shows that of co-precipitation samples. Each figure was standardized in reference to the 592 nm peak. In the results, the spectrum of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition can be observed in each CSH gel. The peak around 618 nm was split into two peaks in the cases of $\text{Ca}/\text{Si} = 1.0, 1.6$ and 1.8 . It is well known that, when Eu(III) is ingested in the CSH structure, its fluorescence emission spectrum shows splitting of the Stark state of the $^7\text{F}_2$ level, which is caused by Eu(III) partly incorporated by CSH gels (e.g., [8]). Consequently, Eu(III) was internally substituted in the CSH gel with a Ca/Si ratio > 1.0 .

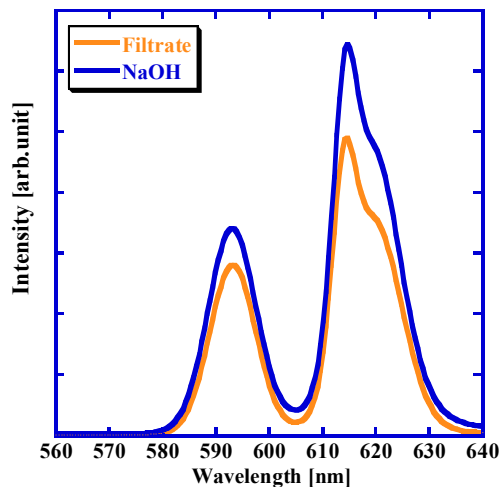


Fig. 3. Fluorescence emission spectra of Eu(III) excited by 390 nm in the absence of CSH gel.

Moreover, in the co-precipitation sample, the peak at 584 nm was remarkably sharp compared to that of the surface sorption samples. According to Pointeau et al. [7], the 584 nm peak is the peak caused by Eu(III) incorporated in the CSH structure, and the 596 nm peak is the peak caused by Eu(III) sorbed on the surface in the form of a complex, etc. Because Eu(III) in the co-precipitation sample is incorporated into the CSH structure in advance, it is confirmed that the 584 nm peak is higher than those of the surface sorption samples.

In addition, in the CSH gel whose Ca/Si ratio is 0.1-0.8, the spectrum at around 618 nm is not split and is similar to that of the filtrate. That is, most Eu(III) seemed hydrolyzed in such condition as the Ca/Si ratio < 1.0 . However, these decay behaviors of the fluorescence emission spectrum were quite different from those obtained from hydrolyzed Eu(III) without CSH gels.

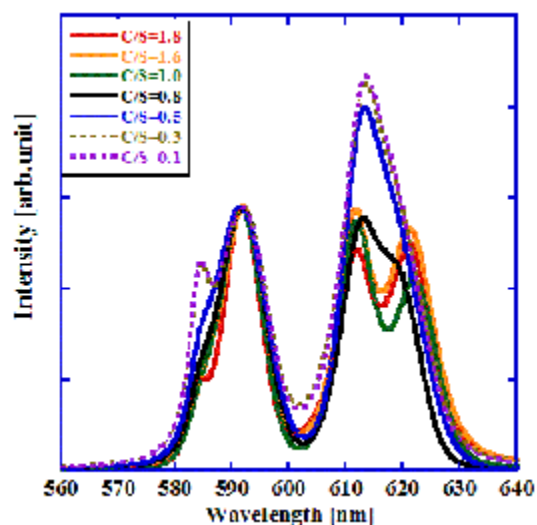


Fig. 4. Fluorescence emission spectra of surface sorption sample (excited by 390 nm) .

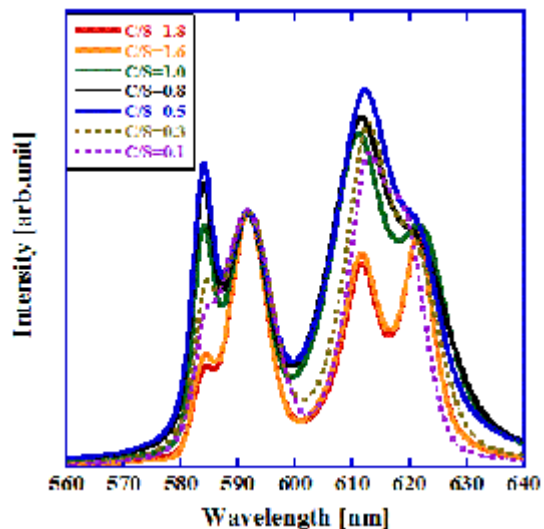


Fig. 5. Fluorescence emission spectra of co-precipitation sample (excited by 390 nm) .

Figure 6 shows the decay curves of fluorescence of the surface sorption samples, and Figure 7 shows those of the co-precipitation sample. As mentioned above, the decay curves of the fluorescence emission spectrum were quite different between the filtrate samples and low Ca/Si ratio samples. That is, low Ca/Si ratio samples underwent slow decay of fluorescence, and their profiles were similar to those of the high Ca/Si ratio samples. The “Filtrate” means a solution filtrated from the suspension of CSH gels (cured for 7 days) by a 0.20 μm membrane filter. Its filtrated solution (pH 11.8) was contacted with a 1 mM Eu(III) solution. Therefore, in the “Filtrate” sample, the majority of added Eu(III) is precipitated as the hydrolyzed type forming the $\text{Eu}(\text{OH})_3$ colloid. Such a fluorescent intensity decreases exponentially with time. However, in Figure 6, the logarithm of the intensity for any CSH sample was obtained not in a linear but a curve. This tendency was also reported in experiments that sorbed Eu on a solid phase and observed fluorescence emission spectra [7, 9].

It is supposed that couples of Eu(III) species containing hydroxide are formed on the surface or in the structure of the solid phase. This could be a reason for that the observed fluorescence decay curves are double or triple exponential curves contrasting with the single exponential curve observed in the filtrate sample. Moreover, as two Eu(III) atoms get close in the solid phase, the energy exchange between Eu(III) atoms becomes possible as a deexcitation path [7, 9]. Such an energy exchange also affects the deexcitation process, so its decay curve is not simply exponential. This energy exchange is more remarkable at higher temperatures [9].

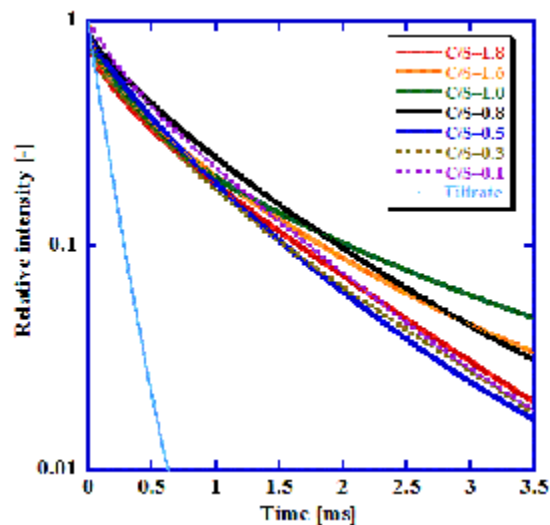


Fig. 6. Fluorescence decay curves of surface sorption sample.

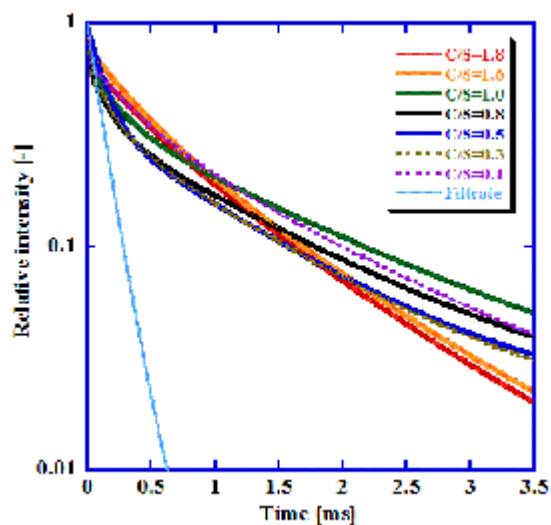


Fig. 7. Fluorescence decay curves of co-precipitation sample.

The fluorescence lifetime is defined as the time when the strength of fluorescence decreases to the e^{-1} time. Therefore, the fluorescence lifetime cannot be strictly defined when the attenuation of fluorescence is not exponential [10]. To evaluate the decay behavior using several exponential components, the time period of attenuation from the e^{-2} -fold to the e^{-3} -fold of the early strength was defined as the 3rd e-folding time, and the fluorescence lifetime was calculated. In this study, it was assumed that the 3rd e-folding time was calculated as a fluorescence lifetime [7, 9]. The fluorescence lifetime (3rd e-folding time) of each sample is shown in Table II.

Table II. Fluorescence lifetime.

Fluorescence lifetime (ms)								
Ca/Si	1.8	1.6	1	0.8	0.5	0.3	0.1	filtrate
surface sorption	0.819	1.047	1.423	1.394	0.913	0.886	1.473	0.11
co - precipitation	0.902	0.944	1.588	1.204	1.247	0.989	1.111	

Each CSH gel has a fluorescence lifetime longer than that of the “Filtrate” sample, so Eu(III) is not only hydrolyzed to form an $\text{Eu}(\text{OH})_3$ colloid, but is also forming a complex on the surface. These results mean that the nuclide is sorbable to CSH gel even with a relatively low Ca/Si ratio <1.0 (the Ca/Si ratio of usual cement is 1.8). Furthermore, since the CSH gel has loose structure with free water, the surface sorption sample would gradually become closer to the co-precipitation sample through a long time period. This suggests that CSH gels, also as a secondary mineral around the repository, retard the migration of RNs. To examine this in detail, we also need to consider the change of the macrostructure of CSH gels, e.g., the change of the BET surface area.

CONCLUSIONS

In this study, the sorption behavior of Eu(III) into CSH gel with a relatively low Ca/Si ratio <1.0 was examined, using the fluorescence emission spectrum and the decay behavior of the fluorescence emission spectrum. As the fluorescence emission spectra were compared, in the surface sorption sample with a high Ca/Si ratio ≥ 1.0 , the spectrum at 618 nm was split into two peaks, meaning that Eu(III) was incorporated by CSH gel. On the other hand, the samples of a relatively low Ca/Si ratio <0.8 showed a spectrum profile similar to that of the "Filtrate" sample. When the decay behaviors of the fluorescence emission spectra were compared, low Ca/Si ratio samples underwent a relatively slow decay of fluorescence, and their profiles were similar to those of high Ca/Si ratio samples. This suggests that low Ca/Si ratio samples involves a chemical reaction forming a complex of Eu(III) on the CSH gel surface. As a result, secondary CSH minerals would also retard the migration of radionuclides at least by the complex forming reaction.

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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. H. SAKAMOTO, K. HAGA, "Chemical behavior and long-term stability of cement, Research of radioactive waste," *J.NUCLEAR FUEL CYCLE AND ENVIRONMENT*, **3**, 81 (1997).
3. K. KOMATU, H. USUI, J. KADOWAKI, Y. NIIBORI, and H. MIMURA, "Permeability Change with Dissolution and Precipitation Reaction induced by Highly Alkaline Plume in Packed Bed with Amorphous Silica Particles", Proc. of 16th Pacific Basin Nuclear Conference (16PBNC), Paper No. P16P1167, 1-6 (2008).
4. D.SUGIYAMA, T. FUJITA, J.A. BERRY, S. J. WILLIAMS "A study of Sorption Mechanism onto Cement Hydrates Isotherm Measurements," *CRIEPI(Central Research Institute of Electric Power Industry) report*, T02025 (2003).
5. J. TITS, K. IJIMA, E. WIELAND, T. TOMURA, G. KAMEI "THE ROLE OF C-S-H PHASES IN THE IMMOBILIZATION OF STRONTIUM AND RADIUM BY CEMENTITIOUS MATERIALS," *29 th International Symposium on the Scientific Basis for Nuclear Waste Management PROGRAM& ABSTRACTS, MRS 2005* 171 (2005).
6. J. TITS, T. STUMPF, T. RABUNG, E. WIELAND, and T. FANGHÄNEL "Uptake of Cm(III) and Eu(III) by Calcium Silicate Hydrates: A Solution Chemistry and Time-Resolved Laser Fluorescence Spectroscopy Study," *Environmental Science & Technology*, **37**, 3568-3573 (2003).
7. I. POINTEAU, B. PIRIOU, M. FEDOROFF, M-G. BARHES, N. MARIMIER, and F.

- FROMAGE “Sorption Mechanisms of Eu^{3+} on CSH Phases of Hydrated Cements,” *Journal of Colloid and Interface Science*, **236**, 252-259 (2001).
8. Y. NIIBORI, M. NARITA, J. KADOWAKI, H. YOSHIKAWA, A. KIRISHIMA, and H. MIMURA, “Sorption Behavior of Europium on Calcium Silicate Hydrates”. Proc. of 16th Pacific Basin Nuclear Conference (16PBNC), Paper No. P16P1075, 1-6 (2008).
 9. B. PIRIOU, M. FEDOROFF, J. JEANJEAN, and L. BERCIS “Characterization of the Sorption of Europium(III) on Calcite by Site-Selective and Time-Resolved Luminescence Spectroscopy,” *Journal of Colloid and Interface Science*, **194**, 440-447 (1997).
 10. Z. TAMURA, T. TABATA, K. YASUDA "Fluorescence analysis," KODANSYA Co., Ltd, Tokyo, Japan (1982).