Fluorescence emission behavior of Eu(III) sorbed on calcium silicate hydrates as a secondary mineral formed without drying process

Yuichi NIIBORI*, Masayuki NARITA*, Akira KIRISHIMA**, Taiji CHIDA* and Hitoshi MIMURA *
*Department of Quantum Science and Energy Engineering, Tohoku University
6-6-01-2, Aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
E-mail: yuichi.niibori@qse.tohoku.ac.jp
**Institute of Multidisciplinary Research for Advanced Materials, Tohoku University
2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

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Abstract
Calcium silicate hydrate (CSH) is a main component of cement-based material required for constructing the geological repository. As in many countries, since the repository in Japan is constructed below water table, we must consider the interaction of radionuclide with cement materials altered around the repository after the backfill. Using fluorescence emission spectra, so far, the authors have investigated the interaction of Eu(III) (as a chemical analog of Am(III)) with CSH gels as a secondary mineral for med without drying process, considering a condition saturated with groundwater. However, in such fluorescence emission behaviors, a deexcitation process of OH vibrators of light water and a quenching effect caused by Eu-Eu energy transfer between Eu atoms incorporated in the CSH gel must be considered. This study examined the fluorescence emission behavior of Eu(III) sorbed on CSH gels, by using La(III) (non-fluorescent ions) as a diluent of Eu(III). Furthermore, CSH samples were synthesized with CaO, SiO$_2$, and heavy water (D$_2$O) as a solvent in order to avoid the obvious deexcitation process of OH vibrators of light water. In the results, the peak around 618 nm was split into two peaks of 613 nm and 622 nm in the cases of Ca/Si=1.0 and 1.6. Then, the peak of 613 nm decreased with increment of Eu(III)/La(III) ratio. This means that the relative intensity of 613 nm is useful to quantify the amount of Eu(III) incorporated in CSH gel. Besides, the decay behavior of the fluorescence emission did not depend on the Eu/La concentration ratio. That is, such a quenching effect is neglectable. Additionally, the fluorescence emission spectra of Eu(III) showed that the state of Eu(III) depended on Ca/Si ratio of CSH. This suggested that there were several sites in CSH to incorporate Eu(III). When CSH is altered, whole cementitious material in repository must be altered forming cracks and leaching some calcium compositions. Therefore, the adsorptive capacity of CSH might also play a key role to retard the migration of nuclides released from the waste body. This study mentioned the fundamental behaviors on the interaction of radionuclides and the altered CSH around the repository.

Key words: Radioactive wastes, Europium, Calcium silicate hydrates, Fluorescence emission spectra

1. Introduction

Particularly when the repository of geological disposal system is located below water table, a large amount of cement materials is required. So far, Federation of Electric Power Companies of Japan (FEPC) and Japan Nuclear Cycle development institute (JNC) (2005) have investigated the impact of cementitious material on the surroundings of the repository. In the results, it was suggested that such cement-based materials form Calcium Silicate Hydrate (CSH) as a secondary mineral around the repository for a long time period exceeding ten thousand years. Such CSH gels undergo relatively low Ca/Si molar ratio (less than 1.0) in a condition saturated with groundwater (e.g., Sugiyama, et al., 2003), Thus, Niibori et al. (2008), (2011) and (2013a, b), Narita et al. (2010), and Funabashi et al. (2012) have examined the
interaction of radionuclides (RNs) and the CSH gels in the solution (with no drying process), by using fluorescence emission decay behaviors. The results suggested that Eu(III) is not only hydrolyzed to form an Eu(OH)$_3$ colloid, but is also forming a complex on the surface of CSH gels or is also incorporated by CSH gels under a condition larger than 10 in pH where the solubility of Eu(III) is very low ($<1 \times 10^{-10}$ M) for equilibration with CSH (Ca/Si>0.5). In such an interpretation, however, we must also consider a quenching effect caused by Eu-Eu energy transfer between Eu atoms incorporated in the CSH gels in the addition to a deexcitation process of OH vibrators of light water. Piriou et al. (1997) and Pointeau et al. (2001) pointed out that, as two Eu(III) atoms get close in the solid phase, the energy exchange between Eu(III) atoms becomes possible as a deexcitation path. Such an energy exchange also affects the deexcitation process.

Based on the authors’ previous works, in this study, the fluorescence emission behavior of Eu(III) sorbed on CSH gels was discussed by using La(III) (non-fluorescent element) as a diluent of Eu(III). Besides, Kimura and Kato (1998) have reported that heavy water to be used as a solvent can suppress a deexcitation process of OH vibrators. Therefore, in this study, the CSH samples were synthesized with CaO, SiO$_2$, and heavy water (D$_2$O) as a solvent in order to avoid an obvious deexcitation process of OH vibrators of light water.

2. Experimental
2.1 Samples
For observing the sorption behavior of Eu(III) onto CSH samples, this study prepared CSH samples with the Ca/Si molar ratio set to 0.5, 1.0 and 1.6, by using glove box saturated with nitrogen gas. Table 1 shows a given combination in order to synthesize each sample with CaO, SiO$_2$, and heavy water (D$_2$O). The liquid/solid weight ratio was uniformly set to 20 ml/g. While Ordinary Portland Cement is around 1.6 (or exceeds 1.6) in Ca/Si molar ratio, it is known that the altered CSH gels become less than 1.0. SiO$_2$ (fumed silica, AEROSIL 300) was obtained from Japan AEROSIL Ltd. The specific surface area of BET (N$_2$ gas) was 300±30 m$^2$/g. The other chemicals were obtained from Wako Pure Chemical Industries Ltd., and were used without further purification.

Table 1 Materials used to synthesize CSH gel.

<table>
<thead>
<tr>
<th>Ca/Si molar ratio</th>
<th>CaO / g</th>
<th>SiO$_2$ / g</th>
<th>D$_2$O water / ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.50</td>
<td>1.07</td>
<td>31.4</td>
</tr>
<tr>
<td>1.0</td>
<td>0.70</td>
<td>0.75</td>
<td>29.0</td>
</tr>
<tr>
<td>1.6</td>
<td>0.80</td>
<td>0.54</td>
<td>26.7</td>
</tr>
</tbody>
</table>

Fig. 1 Experimental Procedures.

2.2 Procedures
The main experimental processes were based on the procedures already reported by the authors (i.e., Niibori, et al. 2008, 2011, Narita, et al., 2010 and Funabashi, et al., 2012) except adding La(III) into the solution in a given combination
of Eu(III) and La(III). The lanthanide ions, such as Eu(III) and La(III), with no change of the outer electron shells undergo the similar chemical properties. Of the lanthanide elements, it is well known that La(III) is non-fluorescence ions. Besides, the fluorescence of Eu(III) ions is caused by the f-f transitions. Therefore, this study selected La(III) which has no electron in 4f-orbital, in order to examine Eu-Eu energy transfer between Eu ions incorporated in the CSH gels. In this study, the stock solutions of Eu(III) and La(III) were prepared with a deuterated nitric acid (DNO₃) solution.

Figure 1 shows the experimental procedures in which the sample does not undergo drying processes. Eu(III) and La(III) were incorporated in CSH by coprecipitation. So far, Niibori et al. (2008) (2011), Narita et al. (2010), and Funabashi et al. (2012) have prepared the two kinds of samples, the surface sorption sample and the coprecipitation sample. These difference was in the timing of the addition of metal ions. That is, in the case of surface sorption sample, the metal ions were added after a given curing-time. On the other hand, in the case of coprecipitation sample the metal ions were added to CSH sample before curing CSH gels. In the results, the interaction of the metal ions and CSH gels without drying processes was mostly similar in the surface sorption sample and the coprecipitation sample. Therefore, this study prepared only so-called “coprecipitation sample” showing a pseudo steady state of surface sorption sample.

The synthesis of each CSH gel sample was conducted in a glove box saturated with nitrogen gas, in order to avoid contact with carbon dioxide (to prevent carbonation as mentioned by e.g., Pardal, et al. (2009)). Niibori et al. (2008) and Shirai et al. (2010) have checked the XRD of the CSH samples. The patterns were mostly similar to that of tobermorite (Honga and Glasser, 1999). However, the patterns are given through drying processes of the CSH samples. Therefore, Funabashi et al. (2012) have furthermore confirmed by using Raman spectra of the CSH samples without drying process whether the contaminant of carbonate exists or not through the experimental procedures. In the results, the Raman spectra did not show any carbonate such as CaCO₃.

Additionally, as shown in Fig. 1, the temperature was kept constant at 298 K. The samples was cured for 60 days (hereinafter is referred to as “the contacting time”) in the sample tube (sealed and gently shaken with 120 strokes/min). After the contact time-period, the samples for analyses were centrifuged with 7,500 rpm during 10 min. The liquid phase was filtrated by 0.20 μm membrane filter. Then, the concentrations of Eu, La, Ca and Si were also measured by inductively-coupled plasma atomic emission spectrometry (ICP-AES). In addition, the pH was measured. Besides, a 3 ml aliquot of the solution with suspension of CSH was pipetted out and its fluorescence emission spectrum and the decay behavior of the fluorescence emission spectrum were monitored. Fluorescence emission spectrum of Eu(III) was obtained by spectro-fluorometer (JASCO, FP-6500). In order to excite Eu(III) in sample solutions, 390 nm xenon lamp was irradiated. Furthermore, the 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.

3. Results and Discussion

Figure 2 shows the fluorescence emission spectra of Eu(III). Each figure was standardized in reference to the 592 nm peak. The spectrum of 3Dₐ→3F₁ transition and 3Dₐ→3F₂ transition can be observed around 590 nm and 618 nm, respectively, in each CSH gel sample. In addition, in the cases of 1.6 and 1.0 in Ca/Si molar ratio, the peak around 618 nm was split into two peaks observed at 613 nm and 622 nm. The previous works (i.e., Tits, et al., 2003, Niibori, et al., 2008, 2011, Narita, et al., 2010 and Funabashi, et al., 2012) have explained that, when Eu(III) is ingested in the CSH structure, its fluorescence emission spectrum shows the splitting of the Stark state of the 3F₂ level. That is, such a splitting is caused by Eu(III) partly incorporated by CSH gels. Furthermore, as shown in Fig. 2, when the concentration ratio of Eu(III) (=[Eu(III)]/[([La(III)]+[Eu(III)])]×10²) increased from 33% to 100%, the peak intensity of 613 nm decreased in comparison with those of 622 nm. Besides, in the cases of Ca/Si ratio 1.0 and 0.5, the peak at 584 nm was relatively sharp compared to that in 1.6. Pointeau et al. have reported that the 584 nm peak also is caused by Eu(III) incorporated in the CSH structure. As shown in Fig. 2, however, the peak intensity at 584 remarkably decreased depending on the addition amount of Eu(III). Since these spectra was standardized in reference to the 592 nm peak, in other words the peak intensity at 584 nm relatively decreased compared to that at 592 nm. In summary, Fig. 2 might suggest that the state of Eu(III) depended on Ca/Si ratio of CSH. The peak at 590 nm split clearly only for the cases of Ca/Si = 1.0 and 0.5. The split of the peak at 618 nm became unclear as Ca/Si ratio decreased. It could be suggested that there was several sites in CSH to incorporate Eu(III).
Figure 3 shows the decay behavior of fluorescence emission spectra of each CSH gel sample. As shown in Fig.3, the decay behavior does not depend on the concentration ratio of Eu(III). This means that such a quenching effect caused by Eu-Eu energy transfer between Eu atoms is negligible in the CSH gels. Furthermore, this study evaluated these fluorescence lifetimes. In general, 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. To evaluate the decay behavior using several exponential components, Piriou et al. (1997) and Pointeau et al. (2001) defined the time period of attenuation from the e⁻¹-fold to the e⁻²-fold of the early strength (i.e., 2nd e-folding time) as a fluorescence lifetime. The same manner was used in this study.

Table 2 shows the fluorescence lifetimes. Here, “filtrate” means a solution filtrated from the suspension of CSH gels by a 0.20 μm membrane filter. Its filtrated solution (pH 11.8) was adjusted to a 1 mM Eu(III) solution by newly adding Eu(III). Therefore, in the “filtrate” sample, the majority of added Eu(III) is precipitated as the hydrolyzed type forming the Eu(OH)₃ colloid. As shown in Table 2, the fluorescence lifetimes in any cases with CSH gels were remarkably exceeded that of “filtrate” sample. This means that Eu(III) becomes more stable through some sorption processes (forming a complex on the surface of CSH gels, and/or being incorporated by CSH gels). Furthermore, the fluorescence lifetimes of 1.6 in Ca/Si molar ratio were larger than those of 1.0 and 0.5 in Ca/Si molar ratio. Besides, as shown in Fig. 2, the fluorescence emission spectra of Eu(III) of 1.6 in Ca/Si molar ratio indicated remarkable splitting to 613 nm and 622 nm in comparison with the other cases of Ca/Si molar ratio<1.0. These might suggest that the CSH gel of Ca/Si=1.6 can more stably incorporate Eu(III) than CSH gels with lower Ca/Si molar ratio. After the contact time-period (60 days), Eu(III) and La(III) were detected in neither solution sample (pH>10.2) filtrated through 0.2 μm membrane filter from the CSH gel samples. Besides, this study confirmed from the concentrations of Ca and Si in filtrated solution after 60 days that Ca/Si molar ratio maintained the initially adjusted ratio.
Table 2 Fluorescence lifetimes (ms).  

<table>
<thead>
<tr>
<th>Eu(III) conc. ratio</th>
<th>Ca/Si molar ratio</th>
<th>CSH free filtrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.6</td>
<td>1</td>
</tr>
<tr>
<td>Eu 100%</td>
<td>2.71</td>
<td>1.65</td>
</tr>
<tr>
<td>Eu 67%</td>
<td>2.18</td>
<td>1.54</td>
</tr>
<tr>
<td>Eu 50%</td>
<td>1.95</td>
<td>1.31</td>
</tr>
<tr>
<td>Eu 33%</td>
<td>1.22</td>
<td>1.68</td>
</tr>
</tbody>
</table>

(*: D₂O was used to adjust CSH gels and each solution of Eu(III) (plus La(III)).)

Figure 4(a) shows the fluorescence decay behaviors of the “filtrate” samples (CSH gel free). For comparison, this study confirmed the fluorescence lifetimes of “filtrate” samples prepared in light water, heavy water and those half-and-half (1:1) water as a solvent. Due to an obvious deexcitation process of OH vibrators of light water, the fluorescence lifetime in the case of light water (0.17 ms) became small compared to that of heavy water (0.42 ms). Furthermore, as mentioned above, Eu(III) in the filtrate samples mainly exists as the hydrolyzed species forming Eu(OH)₃. Fig. 4(a) shows that such a fluorescent intensity decreases exponentially with time even if light water or heavy water is used as a solvent. Besides, Fig. 4(b) shows the fluorescence emission spectra of the filtrate samples. It was confirmed that these filtrate samples (CSH gel free) did not undergo the splitting due to the Stark state of the ⁷F₂ level (as observed in Fig. 2(b)) in fluorescence emission spectra.

Fig. 4 The fluorescence emission decay behaviors of Eu(III) in the “filtrate” samples (with no CSH gel) adjusted by light water, heavy water and those half-and-half water as a solvent (a), and those fluorescence emission spectra (b).

Figure 5 shows an influence of the contact time on the decay behavior of fluorescence emission. Here, the CSH gel samples were adjusted to 1.6 in Ca/Si molar ratio. As shown in Fig. 5, the decay behavior in the case of the contact time-period 30 days became a curve, contrasting with the single exponential decay observed in the filtrate samples. This suggests that plural deexcitation processes affect the decay behavior. On the other hand, in the case of the contact time-period 60 days the fluorescent intensity decreased exponentially with time except relatively initial time. This means that the state of Eu(III) was stabilized in 60 days. Amorphous CSH may incorporate other coexisting ions such as Eu(III) or sorb them by forming a complex on the surface. Actually, Shirai et al. (2010) and Niibori et al. (2013a) have reported that CSH gels can incorporate iodide ions under a wetting condition saturated with groundwater.
4. Conclusions

The fluorescence emission behavior of Eu(III) sorbed on CSH gels were examined, by using La(III) (non-fluorescent element) as a diluent of Eu(III). Besides, in this study, the CSH samples were synthesized with CaO, SiO₂, and heavy water (D₂O) as a solvent in order to avoid an obvious deexcitation process of OH vibrators of light water. Furthermore, this study carried out these experiments with no drying process, considering a condition saturated with groundwater. The results showed that a quenching effect caused by Eu-Eu energy transfer between Eu atoms incorporated in the CSH gel was negligibly small under the condition in the range of 0.5 to 1.6 in Ca/Si molar ratio.

The use of cementitious materials to construct the repository alters the surrounding groundwater up to >10 in pH through a long time-period such as 10⁴ years. Besides, it is well known that, in such a high pH condition, polyvalent ions such as Eu(III) hydrolyze, also partly forming colloids. Such colloids might migrate downstream from the repository. However, this study showed through the detail of fluorescence emission behavior of Eu(III) that CSH gels, even if undergoing a relatively low Ca/Si molar ratio, become stable by forming a complex on the surface of CSH gels, and/or by incorporating polyvalent ions. This suggests the use of cement material, as results, forms a chemical barrier around the repository, because calcium silicate hydrate (CSH) as a second mineral is maintained through a long time-period in which the pH exceeds 10 around the repository. To understand such a barrier mechanism in detail, we need to examine the interactions of CSH gels and radionuclides in more realistic underground conditions.

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