

EFFECTS OF SPECIATION AND CARBONATE ON THE SORPTION OF EU(III) ONTO GRANITE

Min-Hoon Baik[†], Won-Jin Cho, and Pil-Soo Hahn

Korea Atomic Energy Research Institute, Dukjin-Dong 150, Yuseong-Gu, Daejeon 305-353, Korea
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Abstract : An experimental study on the sorption of Eu(III) onto granite was performed as a function of pH in order to investigate the effects of speciation and carbonate on the sorption using a batch procedure. The distribution of Eu(III) species was also calculated both in the aerobic and anaerobic conditions as a function of pH. The sorption of Eu(III) onto granite particles was found to be greatly dependent upon the pH regardless of the atmosphere conditions. The distribution coefficient K_d of Eu(III) for granite was about 2~1000 mL/g in the aerobic condition and 2~1500 mL/g in the anaerobic condition depending on the pH. In the aerobic condition, the sorption of Eu(III) onto granite above pH 8.5 was decreased and this decreased sorption may be due to the formation of anionic ternary Eu(III)-hydroxyl-carbonate complexes in the solution. However, in spite of the formation of the anionic ternary complexes, the sorption of Eu(III) onto granite was not significantly decreased. Therefore, the effect of carbonate on the sorption of Eu(III) onto granite was considered to be insignificant although the speciation of Eu(III) in the solution was greatly affected by the presence of carbonates.

Key Words : europium(III), sorption, speciation, precipitation, carbonate complexes

INTRODUCTION

One of the major tasks in safety assessments for radioactive waste repositories is to predict the radionuclide migration, which takes account of the sorption characteristics of various radionuclides. Thus radionuclide sorption onto geological media is an important part of the overall investigations needed for the safety assessment of a potential site for the disposal of radioactive wastes.¹⁾ In the most of high-level radioactive waste disposal concept being conceived, the wastes will be disposed in an underground facility located at about 500 m below the surface in a crystalline rock. Granite has been considered a representative crystalline rock in Korea when a

safety assessment has been performed for a generic site for high-level radioactive waste disposal.²⁾

Based on laboratory migration experiments of radionuclides in a single fracture, two types of retardation mechanisms were proposed: (1) surface sorption at the fracture walls and (2) diffusion and bulk sorption into the rock matrix.³⁾ There is a large potential for bulk sorption due to the large volumes of rock matrix available relative to fracture surfaces.⁴⁾ Generally speaking, surface sorption may prevail at small timescales, whereas bulk sorption may be dominant at larger geological timescales.⁵⁾ Until now, many sorption experiments for rock materials have also been performed using crushed rocks. Thus, in this study, crushed granite was considered as a sorbing solid medium.

In general, the sorption has been empirically characterized by the distribution coefficient, K_d ,

[†]Corresponding author
E-mail: mhbaik@kaeri.re.kr
Tel: 042-868-2089, Fax: 042-868-8850

which describes the equilibrium partitioning of a solute between the solid and solution phases. A number of sorption studies have been performed in the past, usually with the intention of recommending K_d values for various elements.⁶⁻⁹ In fact, the current approach is to treat K_d as an empirical parameter and K_d is representative only of the specific conditions being studied. Therefore, an understanding of the factors that influence the sorption characteristics is essential when we apply the empirically derived K_d values outside the range of the experimental parameters.

Europium has been considered as an analogue for trivalent lanthanides and actinides (e.g., Am³⁺ and Pu³⁺). It has also some similarities with other common trivalent elements (e.g., Al³⁺ and Fe³⁺).¹⁰ Thus there have been many studies on the thermodynamic chemical behavior of Eu(III) species in an aqueous solution^{11,12} and the sorption of Eu(III) onto various clay minerals¹³⁻¹⁵ and oxides.^{10,16,17} However, only a few of studies have been performed on crystalline rocks such as granite.

Because natural aquatic systems comprise a wide variation of chemical parameters, such as pH, Eh, ionic strength, and CO₂(g) partial pressure, the speciation and precipitation (or solid phase formation) are very sensitive to the aquatic conditions of a given system. This is particularly true for carbonate formation of metal ions with higher oxidation state ($Z \geq 3+$), such as lanthanides and actinides.¹¹ Thus in this study, we investigated the effects of carbonate both on the speciation of Eu(III) in the solution and on the sorption of Eu(III) onto granite.

Therefore, the aims of this study are 1) to determine the K_d values of Eu(III) onto a domestic crushed granite depending on the experimental conditions, 2) to analyze the precipitation and sorption behavior of Eu(III) correlated with the aqueous speciation of Eu(III), and 3) finally to investigate the effects of the carbonate concentration as a function of the pH.

EXPERIMENT

The granite rock used in the study was sampled from a domestic granite quarry site located at Dukjeong-myun, Gyonggi-do. The crushed granite particles were prepared by crushing the bulk granite rock and sieving the crushed particles. The granulometric fraction in the diameter from 0.15 to 0.3 mm was taken for the sorption experiments. Mineralogical composition of the crushed granite rock was determined by the point counter method using a polarizing microscope and an X-ray diffractometer (Philips, MPD). The results are shown in Table 1 and Figure 1. The crushed granite was mainly composed of quartz, plagioclase, K-feldspar, biotite, hornblende, and a small amount of the sphene and opaque phases.¹⁸

Table 1. Mineralogical Composition of the Granite Particles by a Modal Analysis of a Polarized Microscope (1000 Points)

Minerals	Composition (volume %)	
	Section 1	Section2
Quartz	46.8	41.6
Plagioclase	24.2	26.6
K-feldspar	12.4	10.6
Biotite	12.8	16.6
Hornblende	2.2	2.0
Sphene	0.4	1.2
Opaque Phases	1.2	1.4
Total	100.0	100.0

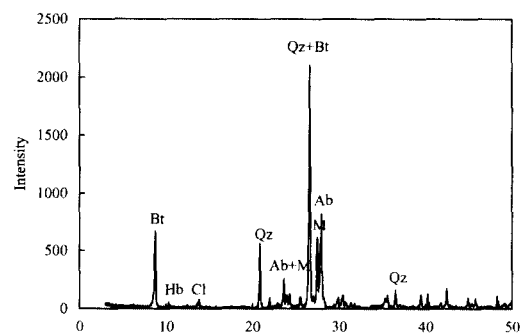


Figure 1. X-ray diffraction result for the granite sample (Hb: hornblende, Cl: chlorite, Qz: quartz, Bt: biotite, Ab: albite (kind of K-feldspar), M: microcline (kind of plagioclase)).

In this study, Eu(III) in the nitrate form ($\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) was used, and the concentration of the uranium was measured by an ICP-MS (Ultramass 700, Varian). All the solutions used were made of AR grade reagents and high purity water with a resistivity of $18.3 \text{ M}\Omega\text{-cm}$ (Milli-Q, Millipore). In order to maintain a constant ionic strength in the system, 0.01 M NaClO_4 was used as an electrolyte. One gram of the crushed granite was transferred to a 30 mL PP (polypropylene) bottle and contacted with 20 mL of a 0.01 M NaClO_4 solution. The solution was adjusted to a desired pH using 0.1 and 1.0 M NaOH or HClO_4 solutions. The pH of each solution was measured by a pH meter (EA-940, Orion). When the pH was stabilized, 10^{-3} M europium stock solution (at pH 3) was added to the flask to achieve an initial europium concentration of 10^{-6} M .

For the aerobic sorption experiment, water-saturated air was bubbled through the solution in order to maintain equilibrium with an ambient atmosphere. The bottle was placed in an automatically temperature controlled shaker to maintain the temperature at 25°C , and was gently shaken at 100 rpm . Anaerobic sorption experiment was performed in a glove box, having the dimensions of $210 \times 80 \times 60 \text{ cm}$, and N_2 gas of a high purity (99.999%) was used as an inert gas (see Figure 2). A column filled with LiF pellets was installed to remove CO_2 from the air in the glove box by circulating the air using a gas-circulating pump. In order to maintain the temperature in the glove box at 25°C , the air was cooled by a cooling water system. The concentration of CO_2 in the glove box was analyzed by GC (DID, HP Agilent) and an appropriate CO_2 -free condition was verified ($C_{\text{CO}_2} < 1.0 \text{ ppm}$ or $P_{\text{CO}_2} < 10^{-6} \text{ atm}$).

The sampled aliquots after reacting the 10^{-6} M Eu(III) solution with granite for 2 weeks were filtered with a syringe filter of $0.22 \mu\text{m}$ pore size (Whatmann) and stored for the analysis of the europium concentration.

Separate experiments were carried out in order to investigate the precipitation behavior of

Figure 2. Schematic diagram of the glovebox filled with inert N_2 gas for the anaerobic sorption experiments ($P_{\text{CO}_2} < 10^{-6} \text{ atm}$).

Eu(III) as a function of the pH, and to quantify the Eu(III) losses on the bottle walls by filtering the 10^{-6} M Eu(III) blank solutions of different pH values through filters of $0.22 \mu\text{m}$ pore size (Whatmann). Uncertainties arising from the Eu(III) losses on the bottle walls and from the analytical error were also taken into account.

RESULTS AND DISCUSSION

Distribution Coefficient

In general, the sorption of radionuclides onto geological media has been empirically characterized by the distribution coefficient K_d (mL/g), which describes the equilibrium partitioning of a solute between the solid phase and the solution phase:

$$K_d = \frac{C_s}{C_q} = \frac{(C_0 - C_q)}{C_q} \cdot \frac{V}{M}$$

where C_s (mol/g) and C_q (mol/mL) are the concentrations of the solute in the solid phase and in the solution phase, respectively, C_0 (mol/mL) is the initial concentration of Eu(III), V is the solution volume (mL) in contact with the granite particles, and M (g) is the mass of the granite

particles.

The contaminants or radionuclides placed in the repository will not travel through the repository at the same rate as the groundwater itself because the contaminants are affected by retardation. The distribution coefficient, K_d , is related to the retardation by the following equation:¹⁹⁾

$$R_d = 1 + \frac{\rho_b}{\varepsilon} K_d$$

where ρ_b (g/cm³) is the dry bulk density of the solid, ε is the porosity of the solid medium, and R_d is the retardation factor of the solid medium. Retardation factor is generally defined as the average migration velocity of a contaminant (V_s) relative to the average groundwater velocity (V_w) according to $R_d = V_w / V_s$.¹⁹⁾ Therefore the average migration velocity of a contaminant in the groundwater will be decreased as the contaminant sorption onto solid surfaces increases.

Speciation and Precipitation of Eu(III)

The chemical speciation of Eu(III) was calculated by the geochemical code MINTEQA2²⁰⁾ with the thermodynamic data from Table 2 in

order to provide information on the probable europium speciation in the solutions depending on the atmospheric conditions.^{12,21)} The calculated distribution of the aqueous and precipitated species of 10⁻⁶ M Eu(III) in the anaerobic condition ($P_{CO_2} < 10^{-6}$ atm) at 25°C is given in Figure 3. The uncomplexed Eu³⁺ dominates in an acidic pH range up to 7. The hydroxyl complexes Eu(OH)₂⁺ and EuOH²⁺ are also present between pH 6 and 8.5. However, in an

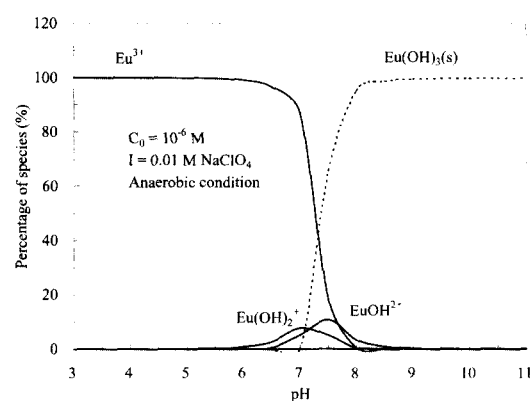


Figure 3. Calculated results of the Eu(III) species in the anaerobic condition ($P_{CO_2} < 10^{-6}$ atm) as a function of the pH.

Table 2. Formation Constants of the Solution and Solid Species of Eu(III)

Reactions	log K (I=0)
$Eu^{3+} + H_2O - H^+ (EuOH^{2+})$	-7.9 ¹²⁾
$Eu^{3+} + 2 H_2O - 2 H^+ (Eu(OH)_2^+)$	-14.9 ¹²⁾
$Eu^{3+} + 3 H_2O - 3 H^+ (Eu(OH)_3(aq))$	-24.1 ¹²⁾
$Eu^{3+} + 4 H_2O - 4 H^+ (Eu(OH)_4^-)$	-36.6 ¹²⁾
$Eu^{3+} + CO_3^{2-} (Eu(CO_3)^+)$	7.9 ¹²⁾
$Eu^{3+} + 2 CO_3^{2-} (Eu(CO_3)_2^-)$	12.2 ⁸⁾
$Eu^{3+} + 3 CO_3^{2-} (Eu(CO_3)_3^{3-})$	14.1 ¹²⁾
$Eu^{3+} + H^+ + CO_3^{2-} (EuHCO_3^{2+})$	12.4 ¹²⁾
$Eu^{3+} + 2 H_2O + CO_3^{2-} - 2 H^+ (Eu(OH)_2CO_3^-)$	-7.6 ¹²⁾
$Eu^{3+} + H_2O + 2 CO_3^{2-} - H^+ (EuOH(CO_3)_2^{2-})$	5.4 ¹²⁾
$Eu^{3+} + 3 H_2O - 3 H^+ (Eu(OH)_3(s))$	-15.1 ²¹⁾
$Eu^{3+} + H_2O + CO_3^{2-} - H^+ (Eu(OH)CO_3(s))$	7.8 ²¹⁾
$2 Eu^{3+} + 3 H_2O + 3 CO_3^{2-} (Eu_2(CO_3)_3 \cdot 3H_2O(s))$	35.0 ²¹⁾
$2 Eu^{3+} + 3 H_2O - 6 H^+ (Eu_2O_3(c))$	-52.4 ²¹⁾
$2 Eu^{3+} + 3 H_2O - 6 H^+ (Eu_2O_3(m))$	-54.0 ²¹⁾

alkaline region above pH 7.5, the precipitated species $\text{Eu}(\text{OH})_3(\text{s})$ is the dominant species.

The distribution of the aqueous species of 10^{-6} M $\text{Eu}(\text{III})$ equilibrated with an ambient air ($P_{\text{CO}_2} = 10^{-3.5}$ atm) at 25°C is shown in Figure 4. The calculated speciation of $\text{Eu}(\text{III})$ in the aerobic condition is quite different from that in the anaerobic condition. The uncomplexed Eu^{3+} dominates at a pH < 6. The carbonate complexed EuCO_3^+ is the dominant aqueous species between pH 6 and 8 and then the anionic ternary $\text{Eu}(\text{III})$ -hydroxyl-carbonate complexes

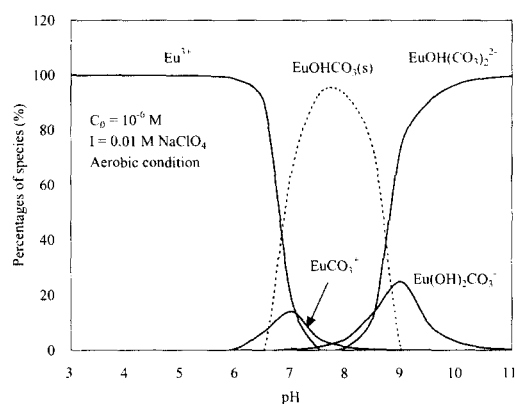


Figure 4. Calculated results of the $\text{Eu}(\text{III})$ species in the aerobic condition ($P_{\text{CO}_2} = 10^{-3.5}$ atm) as a function of the pH.

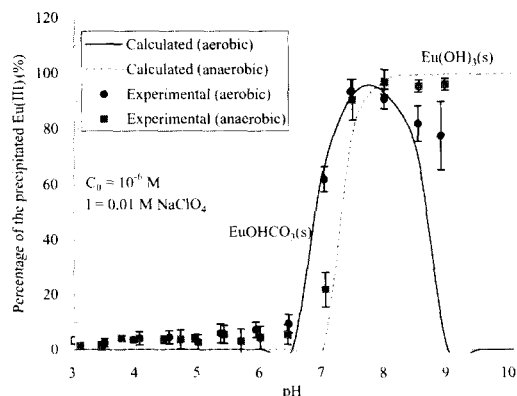


Figure 5. Experimental results of the $\text{Eu}(\text{III})$ precipitation compared with the calculated results in the aerobic ($P_{\text{CO}_2} = 10^{-3.5}$ atm) and anaerobic ($P_{\text{CO}_2} < 10^{-6}$ atm) conditions as a function of the pH (data were obtained in triplicate).

(i.e., $\text{Eu}(\text{OH})_2\text{CO}_3^-$ and $\text{EuOH}(\text{CO}_3)_2^{2-}$) dominate at a pH up to 10. The ternary complex $\text{EuOH}(\text{CO}_3)_2^{2-}$ mainly dominates at pH > 10. Figure 4 also shows that the precipitated solid phase of 10^{-6} M $\text{Eu}(\text{III})$ is $\text{EuOHCO}_3(\text{s})$ in the pH range between pH 6.5 and 9.0 and this precipitated species dominates at this pH range.

Figure 5 shows the result of the precipitation experiments for 10^{-6} M $\text{Eu}(\text{III})$ both in the aerobic ($P_{\text{CO}_2} = 10^{-3.5}$ atm) and anaerobic ($P_{\text{CO}_2} < 10^{-6}$ atm) conditions. The experimental result shows that $\text{Eu}(\text{III})$ does not precipitate in a lower pH below 6 but suddenly starts to precipitate at pH 6 and then attains a maximum precipitation of about 100% at pH 8 in the anaerobic condition and about 95% at pH 7.8 in the aerobic condition, respectively. This result is very consistent with the result of Runde et al.¹¹⁾ showing that the solid species of $\text{Eu}(\text{III})$ investigated by TG/DTA and XRD were $\text{Eu}(\text{OH})\text{CO}_3(\text{s})$ between pH 5 and 7 at 0.03% $\text{CO}_2(\text{g})$ and $\text{Eu}_2(\text{CO}_3)_3(\text{s})$ at 1% and 100% $\text{CO}_2(\text{g})$. Rizkalla and Choppin also suggested that europium was present as a precipitate at a higher pH above 7 and the precipitate was $\text{Eu}(\text{OH})_3(\text{s})$.²²⁾

The experimental data for the $\text{Eu}(\text{III})$ precipitation were also compared with the calculated speciation and is shown in Figure 5. As shown in Figure 5, the experimental data is in good agreement with the result by the speciation calculation. Therefore it can be deduced that europium is present as the uncomplexed ionic species, Eu^{3+} , at a pH < 6 regardless of the presence of $\text{CO}_2(\text{g})$ or carbonates and then the europium starts to precipitate to $\text{Eu}(\text{OH})\text{CO}_3(\text{s})$ in the aerobic condition and to $\text{Eu}(\text{OH})_3(\text{s})$ in the anaerobic condition, respectively, as the pH increases.

Sorption of $\text{Eu}(\text{III})$ onto Granite

Sorption experiments were carried out to investigate the effect of carbonates on the sorption of $\text{Eu}(\text{III})$ onto the granite particles as a function of the pH. As shown in Figure 6, the sorption of $\text{Eu}(\text{III})$ onto granite is greatly

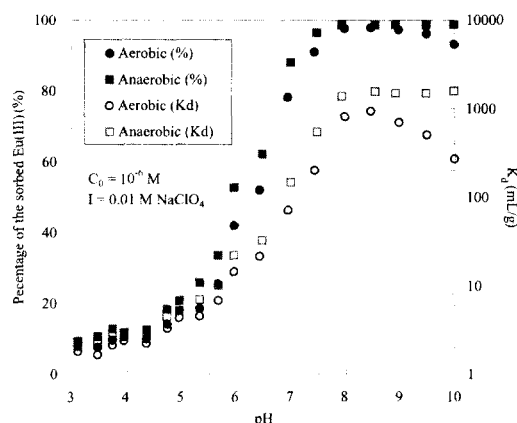


Figure 6. The experimental results of the Eu(III) sorption onto granite in the aerobic ($P_{\text{CO}_2} = 10^{-3.5}$ atm) and anaerobic ($P_{\text{CO}_2} < 10^{-6}$ atm) conditions, respectively, as a function of the pH.

dependent upon the pH. In the anaerobic condition, the sorption of Eu(III) sorbed onto granite increased continuously from pH 3 to pH 8.5 where a maximum K_d value of about 1500 mL/g was attained. The increase of Eu(III) sorption in the acidic and circum-neutral pH regions is related to the cationic europium species in the solution, which shows successively Eu^{3+} , $\text{Eu}(\text{OH})^{2+}$ and EuOH^{2+} with an increasing pH (refer to Figure 3). However, the decreased sorption at a higher pH above 8.5 was not noticed since Eu(III) precipitates in the form of $\text{Eu}(\text{OH})_3(\text{s})$ and does not form carbonate complexes due to the absence of carbonates in the solution.

On the other hand, in the aerobic condition, the sorption of Eu(III) sorbed onto granite also increased continuously from pH 3 to pH 8.5 where a maximum K_d value of about 1000 mL/g was attained. After the maximum sorption was attained, the Eu(III) sorption onto granite slowly decreased with a further increasing pH. The increase of Eu(III) sorption in the acidic and circum-neutral pH regions is also related to the cationic europium species in the solution, which shows successively Eu^{3+} and $\text{Eu}(\text{CO}_3)^+$ (refer to Figure 4). The decreased K_d value above pH 8.5 can be explained by the presence of the anionic ternary complexes which are hard to sorb onto

granite since the anionic ternary Eu(III)-hydroxyl-carbonate complexes (i.e., successively $\text{Eu}(\text{OH})_2\text{CO}_3^-$ and $\text{EuOH}(\text{CO}_3)_2^{2-}$) dominate in the region as predicted in the speciation calculation. Thus the decreased sorption of Eu(III) above pH 8.5 may be due to the increased importance of the anionic ternary Eu(III)-hydroxyl-carbonate complexes in the solution.^{9,11} However, Figure 6 shows that the effect of carbonate on the sorption seems to be insignificant although the speciation and precipitation of Eu(III) is greatly affected by the presence of the carbonates in the solution.

CONCLUSIONS

From the experimental sorption study, the following conclusions are made:

- The sorption of Eu(III) onto granite is greatly dependent upon the pH. The distribution coefficient K_d of Eu(III) for granite is about 2–1000 mL/g in an aerobic condition and 2–1500 mL/g in an anaerobic condition depending on the pH.
- It is considered that the sorption of Eu(III) onto granite is correlated with the europium speciation in the solution and the precipitated species, which depends upon the pH and carbonate concentration.
- In spite of the formation of anionic ternary Eu(III)-hydroxyl-carbonate complexes, the sorption of Eu(III) onto granite is not significantly decreased in the aerobic condition at a higher pH greater than 8.5.
- The effect of carbonate on the sorption of Eu(III) onto granite is considered to be insignificant although the speciation of Eu(III) in the solution is greatly affected by the presence of the carbonates in the solution. This reveals that Eu(III) have a stronger affinity to sorb onto granite than an affinity to form carbonate complexes in the solution. Therefore, Eu(III) migration in granite will be greatly retarded by the sorption onto granite surfaces regardless of the concentration of carbonates.

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REFERENCES

1. Chapman, N. A., McKinley, I. G., and Hill, M. D., *The Geological Disposal of Nuclear Waste*, John Wiley & Sons, Inc., Chichester (1987).
2. Choi, J. W. and Kang, C. H., "Status of the HLW disposal concept development in Korea," *The 2000 Joint Workshop on High - Level Radwaste Disposal Between Korea and Japan*, November 6-7, Daejeon, Korea (2000).
3. Neretnieks, I., Eriksen, T. and Tähtinen, P., "Tracer movement in a single fracture in granitic rock: Some experimental results and their interpretation," *Water Resour. Res.*, **18**, 849-858 (1982).
4. Neretnieks, I., "A note on fracture flow mechanisms in the ground," *Water Resour. Res.*, **19**, 363-379 (1983).
5. Wels, C. and Smith, L., "Retardation of sorbing solutes in fractured media," *Water Resour. Res.*, **30**, 2547-2563 (1994).
6. Vandergraaf, T. T., "Compilation of sorption coefficients for radionuclides on granites and granitic rocks," *Technical Report TR- 120*, Atomic Energy Canada Limited, Pinawa (1982).
7. Andersson, K. and Allard, B., "Sorption of radionuclides on geologic media - A literature survey," *SKB Technical Report TR 83-07*, Swedish Nuclear Fuel and Waste Management Co., Stockholm (1983).
8. McKinley, I. G. and Hadermann, J., "Radionuclide sorption database for swiss safety assessment," *Technical Report NTB 84-40*, Nagra, Würenlingen (1984).
9. Stenhouse, M. and Pöttinger, J., "Comparison of sorption databases used in recent performance assessments involving crystalline host rock," *Radiochim. Acta*, **66/67**, 267-275 (1994).
10. Ledin, A., Kaersson, S., Düker, A., and Allard, B., "The Adsorption of europium to colloidal iron oxyhydroxides and quartz- The importance of pH and an aquatic fulvic acid," *Radiochim. Acta*, **66/67**, 213-220 (1994).
11. Runde, W., Meinrath, G., and Kim, J. I., "A study of solid-liquid phase equilibria of trivalent lanthanide and actinide ions in carbonate systems," *Radiochim. Acta*, **58/59**, 93-100 (1992).
12. Plancque, G., Moulin, V., Toulhoat, P., and Moulin, C., "Europium speciation by time-resolved laser-induced fluorescence," *Anal. Chim. Acta*, **478**, 11-22 (2003).
13. Wang, L., Maes, A., De Cannière, P. and Van Der Lee, J., "Sorption of europium on illite (Silver Hill Montana)," *Radiochim. Acta*, **82**, 223-237 (1998).
14. Lee, D. K., Kim, H. T., Kang, M. J., Hahn, P. S., and Chun, K. S., "Adsorption characteristics of Eu and Th on illite and montmorillonite in aqueous solution," *Hwahak Konghak*, **38(5)**, 753-759 (2000).
15. Coppin, F., Berger, G., Bauer, A., Castet, S., and Loubet, M., "Sorption of lanthanides on smectite and kaolinite," *Chemical Geology*, **182**, 57-68 (2002).
16. Rabung, T., Geckeis, H., Kim, J. I., and Beck, H. P., "Sorption of Eu(III) on a natural hematite: Application of a surface complexation model," *J. Coll. Interf. Sci.*, **208**, 153-161 (1998).
17. Catalette, H., Dumonceau, J., and Ollar, P., "Sorption of Cesium, Barium and Europium on Magnetite," *J. Contam. Hydrol.*, **35**, 151-159 (1998).
18. Baik, M. H. and Hahn, P. S., "An experimental study on the sorption of U(VI) onto Granite," *J. Korean Nucl. Soc.*, **34**, 445-454 (2002).
19. Freeze, R. A. and Cherry, J. A., *Groundwater*, Prentice-Hall, Inc., New Jersey

- (1979).
20. Allison, J. D., Brown, D. S., and Nove-Gradac, K. J., "MINTEQA2/PRODEFA2, A geochemical assessment model for environment systems: Version 3.0 User's Manual," EPA/600/3-91/021, U.S. Environmental Protection Agency, Athens (1991).
 21. Spahiu, K. and Bruno, J., "A selected thermodynamic database for REE to be used in HLNW performance assessment exercises," SKB TR 95-35, Swedish Nuclear Fuel and Waste Management Co., Stockholm (1995).
 22. Rizkalla, E. N. and Choppin, G. R., Handbook of the Physics and Chemistry of Rare Earths, Vol. 15, Gshneidner, K. A. Jr. and Eyring, L. (Eds.), Elsevier North-Holland, New York (1991).