Sorption Properties of Eu(III) onto Granite: Effects of Speciation and Carbonates

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Abstract

An experimental study on the sorption of Eu(III) onto a Korean granite was performed as a function of the 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 assuming equilibrium with the atmosphere (aerobic condition) and controlled atmosphere (anaerobic condition) in the pH range fro 3 to 11. The distribution coefficients, K_d were about 2-1,500 mL/g depending on the experimental conditions. The sorption of Eu(III) onto granite particles was greatly dependent upon the pH. In the aerobic condition, Eu(III) sorption onto granite was not significantly decreased nevertheless formation of anionic ternary Eu(III)-hydroxyl-carbonato complexes (i.e., $Eu(OH)_2CO3^-$ and $EuOH(CO_3)_2^{2-}$) in the alkaline range. Therefore, the effect of carbonate on the sorption of Eu(III) onto granite was insignificant although the speciation of Eu(III) in the solution correlated with solubility and precipitation was affected by the presence of carbonate.

1. 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 in the far-field is an important part of the overall investigations needed for the safety assessment of potential sites for radioactive wastes disposal [1]. In general, the

sorption has been empirically characterized by the distribution coefficient, K_d which describes the equilibrium partitioning of a solute between the solid and solution phases. A number of reviews of sorption literature have been performed in the past, usually with the intention of recommending K_d values for various elements [2-5]. 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 (i.e., Am^{3+} and Pu^{3+}). It has also some similarities with other common trivalent elements (e.g., Al^{3+} and Fe^{3+}) [6]. Thus there has been many studies for thermodynamic chemical behavior of Eu(III) species in the aqueous solution [7, 8] and sorption of Eu(III) onto various clay minerals [9-11] and oxides [6, 12, 13]. However, only a few studies have been performed on crystalline rocks such as granite.

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

2. Experimental

The granite rock used in the study was sampled from a domestic granite quarry site located at Dukjeong-myun, Gyonggi-do, Korea. The crushed granite particles were prepared by crushing the bulk granite rocks and sieving the crushed particles. The granulometric fraction which was smaller than 0.3 mm but bigger than 0.15 mm in diameter was taken for the sorption experiments. Mineralogical composition of the crushed granite rock was determined by point counter methods using electronic microscope and X-ray diffraction. The crushed granite was mainly composed of quarts, plagioclase, K-feldspar, biotite, hornblende, and a small amount of the sphene and opaque phases [14].

In this study, Eu(III) in the nitrate form $(Eu(NO_3)_3 \cdot 5H_2O)$ was used, and the concentration of the uranium was measured by ICP-MS (Varian, Ultramass 700). All

the solutions used were made of AR grade reagents and high purity water with the resistivity of 18.3 $M\Omega-cm$ (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 $NaClO_4$ solution with an appropriate concentration. The flask was adjusted to a desired pH using 0.1 and 1.0 M NaOH or $HClO_4$ solutions, respectively. The pH of each solution was ameasured by Ion Analyzer EA-940 (Orion). When the pH was stabilized, 10^{-3} M $Eu(NO_3)_3 \cdot 5H_2O$ (Aldrich) stock solution (at pH 3) was added to the flask to achieve an initial uranium concentration of 10^{-6} M.

For the aerobic sorption experiments, water-saturated air was bubbled through the solutions in order to maintain equilibrium with ambient atmosphere. The bottle was placed in an automatically temperature controlled shaker to maintain the temperature at 25 ^{o}C, and was gently shaken at 100 rpm. Anaerobic sorption experiments were performed in a glove box, having the dimensions of 210x80x60 cm, and N_2 gas of a high purity (99.999 %) was used as an inert gas (see Fig. 1). 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 ^{o}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 ($<$ 1.0 ppm or $P_{CO_2} < 10^{-6}$ 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 0.22μm pore size (Whatmann) and stored for the analysis of uranium concentration. Separate experiments were carried out in order to investigate the precipitation behavior of Eu(III) as function of pH, and to quantify U(VI) losses on bottle walls by filtering the 10^{-6} M Eu(III) blank solutions with different pH values through filters of 0.22μm pore size (Whatmann). Uncertainties arising from U(VI) losses on bottle walls and from the analytical error were also taken into account.

3. Results and Discussion

3.1. 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 crushed granite particles, and M (g) is the mass of the used granite particles.

3.2. Speciation and Precipitation

The chemical speciation of Eu(III) was calculated by the geochemical code MINTEQA2 [15] with the thermodynamic data from Table 1 in order to provide information on the probable europium speciation in the solutions depending on the atmospheric conditions [8, 16]. The calculated distribution of the aqueous and precipitated species of of 10^{-6} M Eu(III) in the anaerobic condition ($P_{CO_2} \sim 10^{-6}$ atm or < 1.0 ppm) at 25 $^{\circ}$C is given in Fig. 2. The uncomplexed Eu^{3+} dominates at the acidic pH range up to 7. The hydroxyl complexes $Eu(OH)_2^+$ and $EuOH^{2+}$ are also present in the pH between 6 and 8.5. However, in the alkaline pH range above 7.5, the precipitated species $Eu(OH)_3(s)$ is the dominant species.

The distribution of the aqueous species of 10^{-6} M Eu(III) equilibrated with ambient air ($P_{CO_2} = 10^{-3.5}$ atm) at 25 $^{\circ}$C is shown in Fig. 3. The calculated speciation of Eu(III) in the aerobic condition is quite different from that in the anaerobic condition. The uncomplexed Eu^{3+} dominates at pH below 6. The carbonate-complexed $EuCO_3^+$ is the dominant aqueous species in the pH range from 6 to 8 and then the anionic ternary Eu(III)-hydroxyl-carbonato complexes (i.e., $Eu(OH)_2CO_3^-$ and $EuOH(CO_3)_2^{2-}$) in the pH range up to 10. The ternary complex $EuOH(CO_3)_2^{2-}$ dominants at pH above 10. Figure 3 also shows that the precipitated solid phase of 10^{-6} M Eu(III) is $EuOHCO_3(s)$ in the neutral pH range between 6.5 and 9.0 and this precipitated species dominates at the pH region.

Figure 4 shows the result of precipitation experiments for 10^{-6} M Eu(III) both in the aerobic ($P_{CO_2} = 10^{-3.5}$ atm) and anaerobic ($C_{CO_2} < 1$ ppm) conditions. The experimental result shows that Eu(III) does not precipitate in lower pH below 6 but suddenly start to precipitate at pH6 up to pH8 and attains about 100% sorption in

both aerobic and anaerobic conditions. This result is well consistent with the result of Runde et al. [7] showing that the solid species of Eu(III) investigated by TG/DTA and XRD were $Eu(OH)CO_3$(s) between pH5 and pH7 at 0.03% CO_2(g) and $Eu_2(CO_3)_3$(s) at 1% and 100% CO_2(g). Choppin and Rizkalla [17] also suggested that europium was present as a precipitate at higher pH above 7 and the precipitate was $Eu(OH)_3$(s).

Table 1. Formation constants of solution and solid species of Eu(III)

Reaction	log K (I=0)
$Eu^{3+} + H_2O - H^+ \Leftrightarrow EuOH^{2+}$	−7.9 [8]
$Eu^{3+} + 2 H_2O - 2 H^+ \Leftrightarrow Eu(OH)_2^+$	−14.9 [8]
$Eu^{3+} + 3 H_2O - 3 H^+ \Leftrightarrow Eu(OH)_3$(aq)	−24.1 [8]
$Eu^{3+} + 4 H_2O - 4 H^+ \Leftrightarrow Eu(OH)_4^-$	−36.6 [8]
$Eu^{3+} + CO_3^{2-} \Leftrightarrow Eu(CO_3)^+$	7.9 [8]
$Eu^{3+} + 2 CO_3^{2-} \Leftrightarrow Eu(CO_3)_2^-$	12.2 [8]
$Eu^{3+} + 3 CO_3^{2-} \Leftrightarrow Eu(CO_3)_3^{3-}$	14.1 [8]
$Eu^{3+} + H^+ + CO_3^{2-} \Leftrightarrow EuHCO_3^{2+}$	12.4 [16]
$Eu^{3+} + 2 H_2O + CO_3^{2-} - 2 H^+ \Leftrightarrow Eu(OH)_2CO_3^-$	−7.6 [8]
$Eu^{3+} + H_2O + 2 CO_3^{2-} - H^+ \Leftrightarrow EuOH(CO_3)_2^{2-}$	5.4 [8]
$Eu^{3+} + 3 H_2O - 3 H^+ \Leftrightarrow Eu(OH)_3$(s)	−15.1 [16]
$Eu^{3+} + H_2O + CO_3^{2-} - H^+ \Leftrightarrow Eu(OH)CO_3$(s)	7.8 [16]
$2 Eu^{3+} + 3 H_2O + 3 CO_3^{2-} \Leftrightarrow Eu_2(CO_3)_3 \cdot 3H_2O$(s)	35.0 [16]
$2 Eu^{3+} + 3 H_2O - 6 H^+ \Leftrightarrow Eu_2O_3$(c)	−52.4 [16]
$2 Eu^{3+} + 3 H_2O - 6 H^+ \Leftrightarrow Eu_2O_3$(m)	−54.0 [16]

The the experimental data for Eu(III) precipitation were also compared with the calculated speciation and shown in Fig. 4. As shown in the Fig. 4, the experimental

data are in agreement with data by the speciation calculation. Therefore it can be deduced that europium is present as the uncomplexed ionic species, Eu^{3+}, in the acidic pH range lower than pH6 regardless of the presence of $CO_2(g)$ or carbonates and then the europium starts to precipitate to $Eu(OH)CO_3(s)$ at the aerobic condition and to $Eu(OH)_3(s)$ at the anaerobic condition, respectively, as the solution pH increases.

3.3. Sorption

Sorption experiments were carried out to investigate the effect of carbonates on the sorption of Eu(III) onto the granite particles as a function of pH. As shown in Fig. 5, the sorption of Eu(III) onto granite are greatly dependent upon pH. In the anaerobic condition, the sorption of Eu(III) sorbed on granite increased continuously from pH3 to pH8.5 where a maximum K_d value about 1,500 mL/g was attained. The increase of Eu(III) sorption in the acid region is related with the cationic europium species in the solution, which shows successively Eu^{3+}, $Eu(OH)^{2+}$ and $EuHO^{2+}$ with increasing pH (refer Fig. 2). However, the decreased sorption at higher pH above 8.5 was not noticed since Eu(III) precipitates in the form of $Eu(OH)_3(s)$ and do 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 on granite also increased continuously from pH3 to pH8.5 in which a maximum K_d value about 1,000 mL/g was attained. After the maximum sorption was attained, the Eu(III) sorption onto granite slowly decreased with further increasing pH. The increase of Eu(III) sorption in the acidic region is also related with the cationic europium species in the solution, which shows successively Eu^{3+} and $Eu(CO_3)^+$ (refer Fig. 3). The decreased K_d value above pH8.5 can be explained by the presence of anionic ternary complexes which hard to sorb onto granite since the anionic ternary Eu(III)-hydroxyl-carbonate complexes (i.e., successively $Eu(OH)_2CO_3^-$ and $EuOH(CO_3)_2^{2-}$) dominate in the region as predicted in the speciation calculation. Thus the decreased sorption of Eu(III) in the higher alkaline pH is due to the increased importance of the anionic ternary Eu(III)-hydroxyl-carbonate complexes in the solution [8, 10]. However, Fig. 5 shows that the effect of carbonate on the sorption is not significant although the speciation and precipitation of Eu(III) is greatly affected by the presence of carbonates in the solution.

4. Conclusions

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

- The distribution coefficient K_d of Eu(III) for granite was about 2–1,000 mL/g in the aerobic condition and 2–1,500 mL/g in the anaerobic condition depending on the pH.
- It was noticed that the sorption of Eu(III) onto granite was correlated with the europium speciation in the solution and precipitated species, which depends on the pH and carbonate concentrations.
- In the aerobic condition, Eu(III) sorption onto granite was decreased by the formation of anionic ternary Eu(III)-hydroxyl-carbonate complexes in the higher pH above 8.5.
- The sorption of Eu(III) onto granite was greatly dependent upon pH. However, the effect of carbonate on the Eu(III) sorption onto granite was not significant although the speciation and precipitation of Eu(III) was greatly affected by the presence of carbonates in the solution.
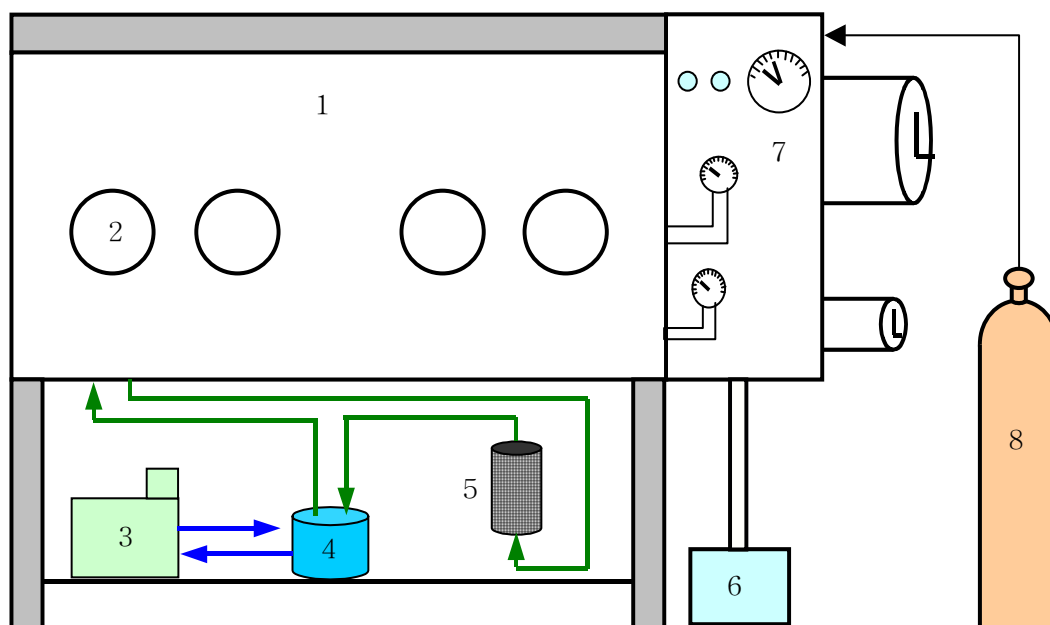
Acknowledgement

References

1. N.A. Chapman, I.G. McKinley, and M.D. Hill, The Geological Disposal of Nuclear Waste, John Wiley & Sons, Inc., Chichester (1987).
2. T.T. Vandergraaf, Compilation of Sorption Coefficients for Radionuclides on Granites and Granitic Rocks, Atomic Energy Canada Limited, Technical Report TR-120 (1982).
3. K. Andersson and B. Allard, Sorption of Radionuclides on Geologic Media - A Literature Survey, Swedish Nuclear Fuel and Waste Management Co., SKB Technical Report TR 83-07(1983).
4. I.G. McKinley and J. Hadermann, Radionuclide Sorption Database for Swiss Safety Assessment, Nagra Technical Report NTB 84-40 (1985).

5. M. Stenhouse and J. Pöttinger, "Comparison of Sorption Databases Used in Recent Performance Assessments Involving Crystalline Host Rock," Radiochim. Acta, 66/67, 267-275 (1994).

6. A. Ledin, S. Kaersson, A. Düker, and B. Allard, "The Adsorption of Europium to Colloidal Iron Oxyhydroxides and Quartz-The Importance of pH and an Aquatic Fulvic Acid," Radiochimica Acta, 66/67, 213-220 (1994).

7. W. Runde, G. Meinrath, and J. I. Kim, "A Study of Solid-Liquid Phase Equilibria of Trivalent Lanthanide and Actinide Ions in Carbonate Systems," Radiochimica Acta, 58/59, 93-100 (1992).

8. G. Plancque, V. Moulin, P. Toulhoat, and C. Moulin, "Europium Speciation by Time-Resolved Laser-Induced Fluorescence," Analytica Chimica Acta, 478, 11-22 (2003).

9. L. Wang, A. Maes, P. De Cannière, and J. van der Lee, "Sorption of Europium on Illite (Silver Hill Montana)," Radiochimica Acta, 82, 223-237 (1998).

10. D.K. Lee, H. T. Kim, M.J. Kang, P.S. Hahn, and K.S. Chun, "Adsorption Characteristics of Eu and Th on Illite and Montmorillonite in Aqueous Solution," Hwahak Konghak, 38(5), 753-759 (2000).

11. F. Coppin, G. Berger, A. Bauer, S. Castet, and M. Loubet, "Sorption of Lanthanides on Smectite and Kaolinite," Chemical Geology, 182, 57-68 (2002).

12. T. Rabung, H. Geckeis, J.I. Kim, and H. P. Beck, "Sorption of Eu(III) on a Natural Hematite: Application of a Surface Complexation Model," J. Coll. Interf. Sci., 208, 153-161 (1998).

13. H. Catalette, J. Dumonceau, and P. Ollar, "Sorption of Cesium, Barium and Europium on Magnetite," J. Conta. Hydrol., 35, 151-159 (1998).

14. M.H. Baik and P.S. Hahn, "An Experimental Study on the Sorption of U(VI) onto Granite," J. Korean Nucl. Soc., 34, 445-454 (2002).

15. J.D. Allison, D.S. Brown and K.J. Novo Gradac, MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environment Systems: Version 3.0 User's Manual, U.S. Environmental Protection Agency, EPA/600/3-91/021, Athens (1991).

16. K. Spahiu and J. Bruno, A Selected Thermodynamic Database for REE to Be Used in HLNW Performance Assessment Exercides, Swedish Nuclear Fuel and Waste Management Co., SKB TR 95-35 (1995).

17. G.R. Choppin and E.N. Rizkalla, Handbook of the Physics and Chemistry of Rare Earths, K. A. Jr. Gshneidner and L. Eyring, eds., North-Holland Pub. (1994).

Fig. 1. Schematic diagram of the glove-box filled with inert N_2 gas for the anaerobic sorption experiments ($P_{CO_2} \sim 10^{-6}$ atm or < 1.0 ppm).

1. Front acryl panel
2. Glove
3. Cooling water circulator
4. Gas circulating pump
5. CO_2 trap column
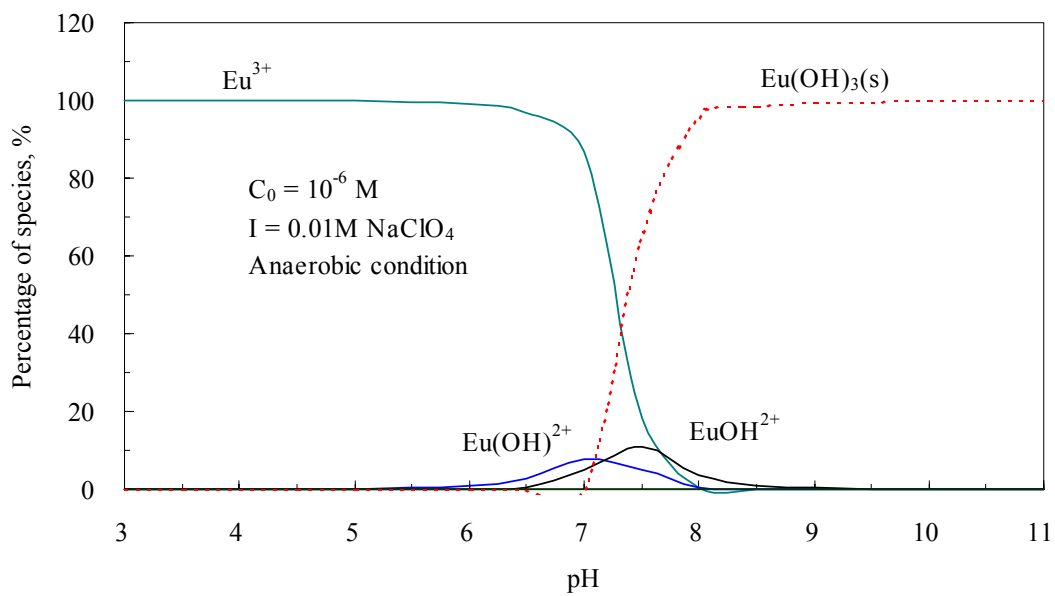6. Vacuum pump
7. Pressure control panel
8. N_2 gas tank

Fig. 2. Calculated results of Eu(III) species in the anaerobic condition ($P_{CO_2} \sim 10^{-6}$ atm) as a function of pH.
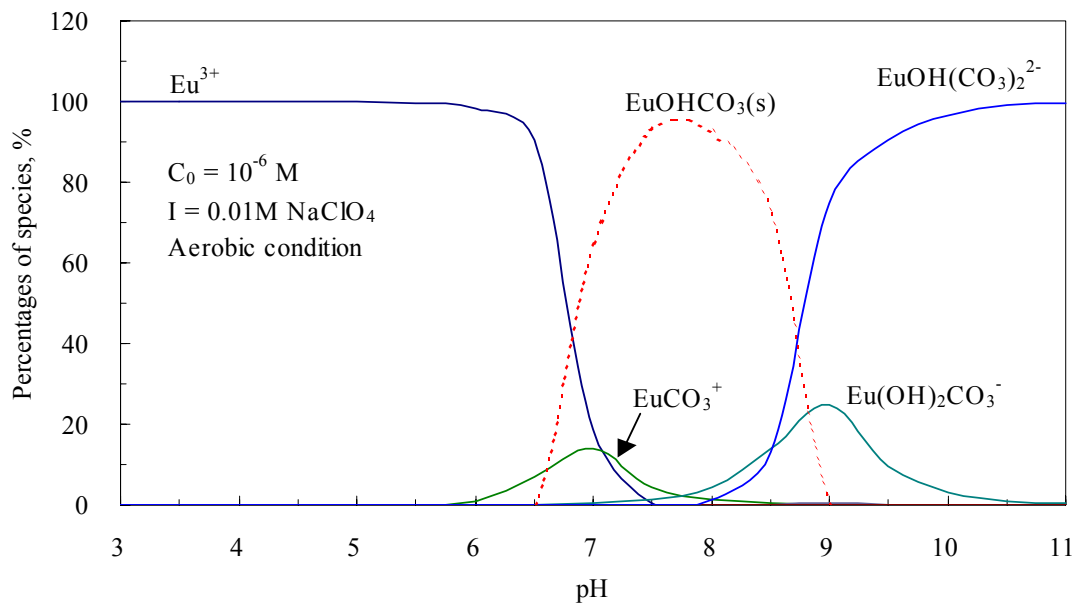

Fig. 3. Calculated results of Eu(III) species in the aerobic condition ($P_{CO_2} = 10^{-3.5}$ atm) as a function of pH.
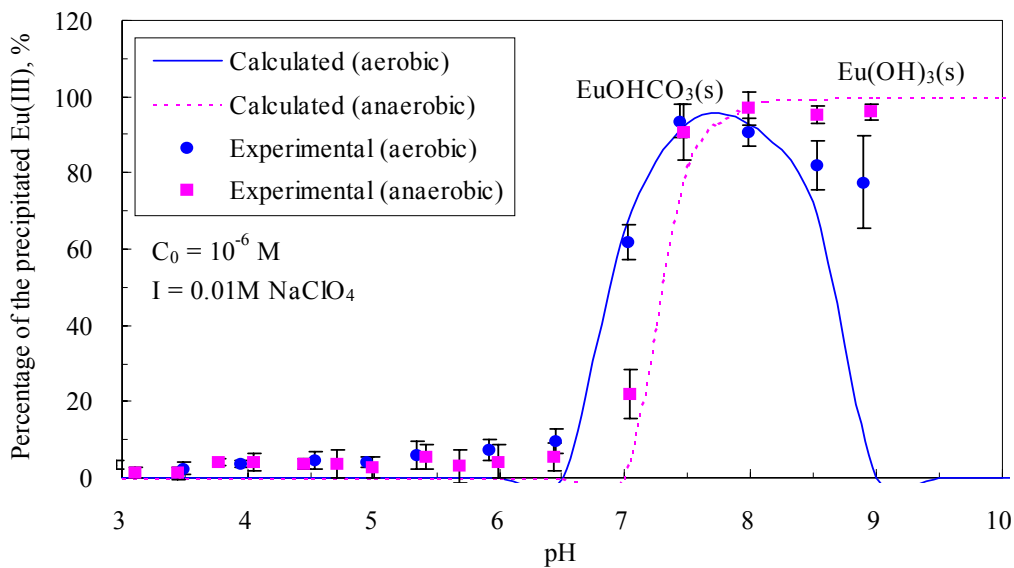
Fig. 4. Experimental results of Eu(III) precipitation compared with the calculated results in the aerobic ($P_{CO_2}=10^{-3.5}$ atm) and anaerobic ($P_{CO_2}\sim10^{-6}$ atm) conditions as a function of pH.
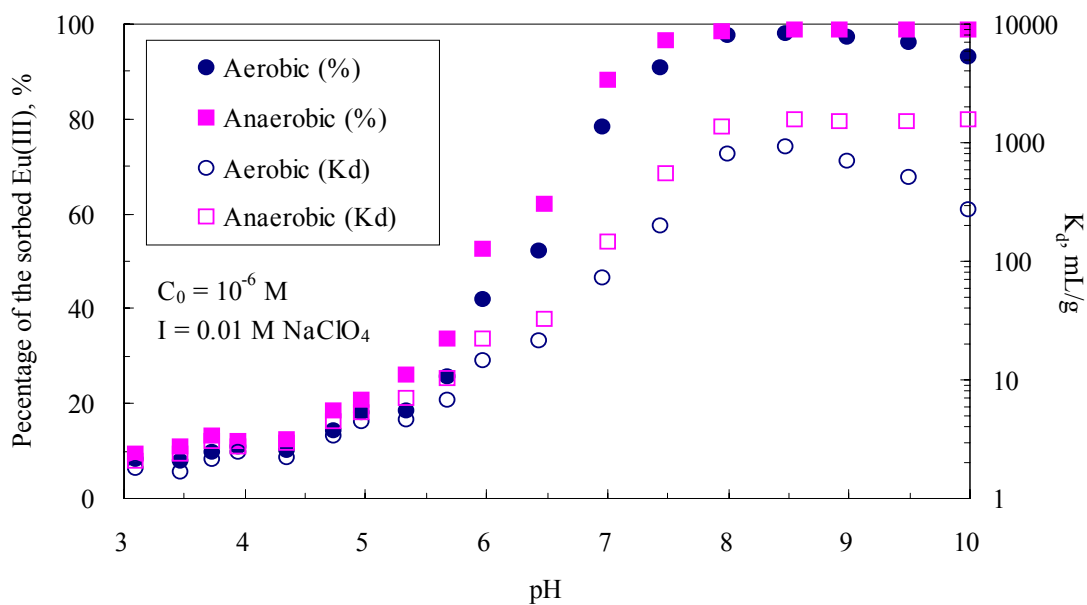

Fig. 5. The experimental results of Eu(III) sorption onto granite in the aerobic and anaerobic conditions as a function of pH.