Sorption of Plutonium on a Biotite Mineral

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It is necessary to obtain the data of some parameters concerning migration behavior of radionuclides in underground water for the safety assessment of radioactive waste disposal. Sorption and desorption experiments were carried out by using tracer amount of plutonium on biotite in a granitic rock. In this study, pH dependence of distribution coefficients of plutonium on a biotite mineral were measured. The following results are obtained;

(1) The biotite has the pH buffer capacity at around pH 5.

(2) Plutonium sorption rate was fast around pH 6 but slow at lower pH than 5.

(3) The 95 percent of plutonium was sorbed on biotite at around pH 5.

(4) The 10 to 30 percent of sorbed plutonium in biotite was desorbed with 1N KCl, the 50 to 60 percent with 1N HNO3.

(5) The rest of plutonium sorbed in biotite could not be desorbed even with 1N HNO3.

(6) The neutral plutonyl hydroxide could be an important species sorbed on the biotite.

1. Introduction

It is necessary to obtain the data of some parameters concerning migration behavior of radionuclides in underground water for the safety assessment of radioactive waste disposal. Especially, there are few sorption data for actinide elements.

Granite is a candidate formation for high-level radioactive waste disposal and exists broadly in Japan. After radionuclides release from a repository, the granite formation would be the last barrier to retard the migration of radionuclides, especially, long-life ones. There are some retardation mechanism for migration of radionuclides in such a geological media; adsorption on surfaces of rocks, diffusion into rocks (matrix diffusion), and so on. Authors obtained some results for migration behavior of uranium in granite [1,2,3,4] ; (1) there are many fissures of several microns in granite, (2) uranium can diffuse into the granite through the fissures, (3) uranium are sorbed mostly in biotite mineral on a surface, (4) the neutral uranyl hydroxide could be an important species for sorption and (5) biotites in the granite are interconnected by the fissures and can give a contribution for sorption of uranium. There are some other reports that biotite has the highest sorption coefficient for many kinds of elements in most of pH range [5,6,7]. In this study, pH dependence of distribution coefficients of plutonium on a biotite mineral were measured.

2. Experimental

The plutonium used in this experiment was 15 kBq of [236]Pu that was made and separated from [237]Np irradiated with high energy X-ray produced by bremsstrahlung in Tohoku university electron LINAC. The plutonium was dissolved in a nitric acid solution and was divided into 8 solutions of 30 mL. The pH of each solution was adjusted at a pH of interest between 3 and 10 by using 0.01 N of HNO3 or 0.01N of NaOH.

Korean granite block was crushed into powder. Then biotite powder (mesh 32 - 60) was collected from the granite powder by using a strong magnet. Hundred grams of the biotite powder were washed with 2000mL of 1N HCl for a week and were rinsed twice with 2000mL of deionized water for a week. This HCl treatment was necessary to remove iron oxides and oxyhydroxides from the biotite powder [4].

The sorption experiments were conducted by contacting 1.0 g of biotite with 30 mL of plutonium solutions in polypropylene bottles for 7 days to 7 months at room temperature. Control experiment consisting plutonium solution without biotite was used to determine potential losses of plutonium to the container wall. After adding biotite powders, 0.2 mL aqueous samples were taken from each mixture to measure plutonium concentration with liquid scintillation counter. The pH of solutions were measured at every sampling time.

The desorption experiments were conducted by sequential extractions with 30 mL of deionized water, 1N KCl, 1N HNO3 from 1.0 g of biotite powder after contact with 30 mL of plutonium solutions.

3. RESULTS AND DISCUSSION

3-1 The pH change in the solutions

Since biotite has the pH buffer capacity, the pH of the solutions should be measured before and after putting biotite into the solutions. The pH change in the solutions are shown in Fig. 1. The pH of solutions above pH 5 dropped suddenly just after adding biotite powders into the solutions, then remained at each pH for few days. In the case of B06, the pH was increased by the addition of base to raise the pH at 90 hours after adding biotite powder. The pH in most of the solutions became around 5 after 7 months because of the buffer capacity of biotite.
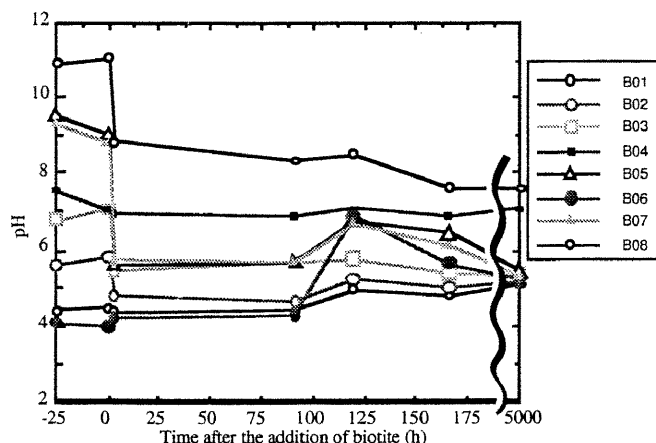

Fig. 1. The pH change in the solutions.

3-2 The plutonium concentration change in the solutions

The plutonium concentration change in the solutions are shown in Fig. 2. The largest change of plutonium concentration was observed in B03 which pH was around 7. The smallest change was in B01 which pH around 5. In the case of B06, the plutonium concentration dropped suddenly at 90 hours after adding biotite because the pH changed from 5 to 7 by addition of base. It means that strong sorption of plutonium in biotite occurred between pH 5 and 7.
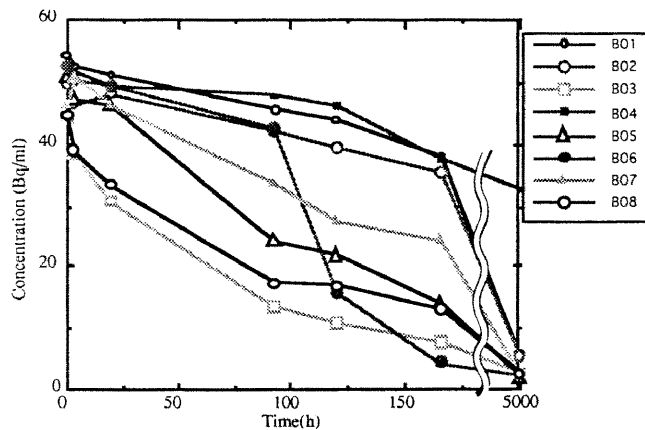

Fig. 2. The plutonium concentration change in the solutions.

3-3 The pH dependence of sorbed plutonium in biotite

The pH dependence of sorbed plutonium in biotite after 90 hours are shown in Fig. 3. Sorption rate of plutonium in biotite was fast at around pH 6. The percentage of sorbed plutonium was also high even if the pH of the solution is as high as 8 and decreased in higher pH.
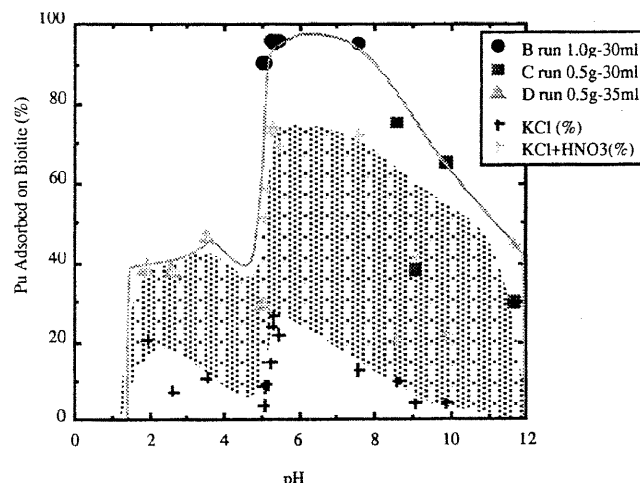

Fig. 3. The pH dependence of sorbed plutonium in biotite.

3-4 The estimation of aqueous plutonium speciation

Aqueous plutonium speciation is illustrated in Fig.4 by using thermodynamic date by P.L.Brown [8] listed in Table 1. Dominant species in solution are $PuO2^+$ and $PuO2^{2+}$ in low pH, $PuO2OH^+$, $PuO2(OH)2$ and $PuO2(OH)3^-$ in middle pH, $PuO2(CO3)2^{3-}$, $PuO2(CO3)3^{4-}$ and $Pu(CO3)5^{6-}$ in high pH. $PuO2^+$ and $PuO2(CO3)2^{3-}$ are the species of penta-valence plutonium. It is confirmed by solvent extraction analysis that there was no species of penta-valence plutonium in the solution used in this study. A comparison of aqueous plutonium speciation and the sorption results indicated that the neutral plutonyl hydroxide could be an important species sorbed on the biotite. In lower pH range, plutonyl ion could be also an important species sorbed on the biotite.

Table 1. Thermodynamic date of plutonium used for estimation of plutonium speciation

| Reactions	log K
$2H2O+Pu^{4+}=4H^{+}+PuO2^{+}+e^{-}$	-18.597
$PuO2^{+}=PuO2^{2+}+e^{-}$	-16.197
$H2O+Pu^{4+}=H^{+}+PuOH^{3+}$	-1.640
$2H2O+Pu^{4+}=2H^{+}+Pu(OH)2^{2+}$	-3.920
$H2O+PuO2^{+}=H^{+}+PuO2OH$	-10.940
$H2O+PuO2^{2+}=H^{+}+PuO2OH^{+}$	-5.590
$3H2O+Pu^{4+}=3H^{+}+Pu(OH)3^{+}$	-3.920
$2H2O+PuO2^{2+}=2H^{+}+PuO2(OH)2$	-11.740
$2H2O+PuO2^{+}=2H^{+}+PuO2(OH)2^{-}$	-22.730
$4H2O+Pu^{4+}=4H^{+}+Pu(OH)4$	-10.010
$3H2O+PuO2^{2+}=3H^{+}+PuO2(OH)3^{-}$	-18.330
$3H2O+PuO2^{+}=3H^{+}+PuO2(OH)3^{2-}$	-35.250
$5H2O+Pu^{4+}=5H^{+}+Pu(OH)5^{-}$	-13.730
$4H2O+PuO2^{2+}=4H^{+}+PuO2(OH)4^{2-}$	-25.300
$4H2O+PuO2^{+}=4H^{+}+PuO2(OH)4^{3-}$	-48.440
$6H2O+Pu^{4+}=6H^{+}+Pu(OH)6^{2-}$	-17.880
$5H2O+PuO2^{2+}=5H^{+}+PuO2(OH)5^{3-}$	-32.630
$5H2O+PuO2^{+}=5H^{+}+PuO2(OH)5^{4-}$	-62.280
$CO3^{2-}+Pu^{4+}=PuCO3^{2+}$	12.150
$CO3^{2-}+PuO2^{2+}=PuO2CO3$	8.080
$CO3^{2-}+PuO2^{+}=PuO2CO3^{-}$	4.280
$2CO3^{2-}+Pu^{4+}=Pu(CO3)2$	23.240
$2CO3^{2-}+PuO2^{2+}=PuO2(CO3)2^{2-}$	15.210
$2CO3^{2-}+PuO2^{+}=PuO2(CO3)2^{3-}$	7.290
$3CO3^{2-}+Pu^{4+}=Pu(CO3)3^{2-}$	33.530
$3CO3^{2-}+PuO2^{2+}=PuO2(CO3)3^{4-}$	21.620
$3CO3^{2-}+PuO2^{+}=PuO2(CO3)3^{5-}$	9.280
$4CO3^{2-}+Pu^{4+}=Pu(CO3)4^{4-}$	43.110
$4CO3^{2-}+PuO2^{2+}=PuO2(CO3)4^{6-}$	27.440
$4CO3^{2-}+PuO2^{+}=PuO2(CO3)4^{7-}$	10.350
$5CO3^{2-}+Pu^{4+}=Pu(CO3)5^{6-}$	52.090
$5CO3^{2-}+PuO2^{2+}=PuO2(CO3)5^{8-}$	32.710
$5CO3^{2-}+PuO2^{+}=PuO2(CO3)5^{9-}$	10.560
$6CO3^{2-}+Pu^{4+}=Pu(CO3)6^{8-}$	60.360
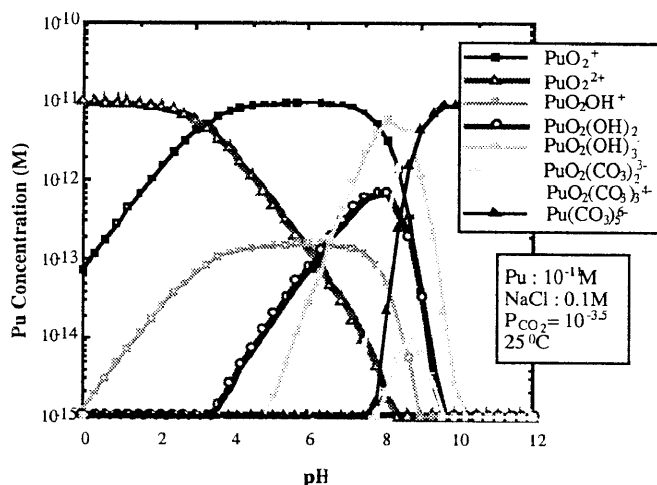
Fig.4 Estimated aqueous plutonium speciation.

3-5 The results of desorption experiments

The amount of plutonium desorbed from the biotite samples are also shown in Fig. 3. The 10 to 30 percent of sorbed plutonium in biotite was desorbed with 1N KCl, the 50 to 60 percent with 1N HNO3 and the rest could not be desorbed even with 1N HNO3.

4. CONCLUSION

(1) The biotite has the pH buffer capacity at around pH 5.

(2) Plutonium sorption rate was fast around pH 6 but slow at lower pH than 5.

(3) The 95 percent of plutonium was sorbed on biotite at around pH 5.

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(5) The rest of plutonium sorbed in biotite could not be desorbed even with 1N HNO3.

(6) The neutral plutonyl hydroxide could be an important species sorbed on the biotite.

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