Study of Pu(IV) and Am(III) sorption to clay minerals: laboratory experiments and modeling

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Summary. Sorption of Pu(IV) and Am(III) to natural clay from a mixture of synthetic rainwater – cement water was studied by batch and sequential extraction experiments as a function of pH and ionic strength. These experiments were intended to simulate the effect of cement dissolution, causing the release of K+, Ca2+ and other cations from solidified radioactive waste into the aqueous phase. The results indicated a complex sorption behavior of the elements studied. It was found that iron oxides play an important role in the uptake of Pu(IV), whereas ion exchange and CaCO3 are mainly responsible for the binding of Am(III) on the clay. Simplified sorption experiments were conducted with clay minerals and iron oxides, using 0.01 and 0.1 mol/L NaNO3 as background electrolyte under an Ar atmosphere, for a better understanding of the sorption mechanisms. The experimental data were interpreted using the combination of surface complexation and ion-exchange models.

1. Introduction

Natural clay minerals can play an important role in retardation and transport of radionuclides. Iron oxide coatings are common components of natural minerals. They can also be formed by corrosion of containers in the waste repositories. Sorption of Pu, as well as of other actinides, depends on many factors such as the type of mineral, pH and redox potential [1, 2]. Recently, significant efforts were made to study the interaction of actinides with various matrices by different methods which resulted in enhanced understanding of their sorption mechanisms to naturally occurring minerals [3]. High concentrations of sorbed Pu were found associated with smectite and Mn oxide fracture minerals. Sorption of Pu to Fe-rich regions was not observed. In a similar experiment in which Tuff was used, Pu was concentrated in the zones of altered orthopyroxenes. These zones contained Fe-rich amorphous materials [4–6]. Later, Pu was mostly found associated with bodies of smectite and Mn oxides but it was not associated with the hematite and other Fe-rich bodies [7]. Sorption behavior of actinides was mainly studied in simple systems with clay minerals (bentonite, kaolinite and montmorillonite) [8–10] while complex natural systems were not studied with sufficient detail and data for these systems were mainly derived from environmental observations [11, 12].

Data obtained from natural environmental samples using sequential extraction (SE) techniques showed a predominant association of Pu isotopes with natural organic matter and iron oxides, whereas less than 1% of Pu was bound to Mn oxides [13–16]. It is well known that plutonium can exist in the aqueous environment in five different oxidation states as ions Pu(III), Pu(IV), Pu(V), Pu(VI), Pu(VII), represented by the ions Pu3+, Pu4+, PuO22+, PuO23+ and PuO2− respectively. Pu(VI) is not considered as a stable species in the natural environment. At near-neutral pH levels and in oxic waters, Pu(III) is rapidly oxidized to Pu(IV) [17, 18]. It is generally accepted that the dominant oxidation states in oxic waters are Pu(IV), Pu(V) and Pu(VI), whereas in anoxic waters Pu(III) is present and may become the dominant soluble species [18, 19]. However, recent studies have indicated transformation of Pu oxidation states through interactions with surfaces of iron- and manganese-bearing minerals, humic acids and bacteria. [3, 18–22]. Banik et al. demonstrated that Pu(VI) can be reduced by Aldrich humic acid and Goreleben fulvic acid to Pu(IV) and Pu(III) within a several weeks. [9]. In groundwater, containing humic substances, Pu was found mainly as Pu(III) and Pu(IV). [23].

The first observation of Pu(III) in natural sediments exposed to air was published in 2007 by Kaplan et al. On the basis of lysimetric experiments with well-defined solid sources of Pu(III) (PuCl3), Pu(IV) (Pu(NO3)4 and Pu2(C2O4)3), and Pu(VI) (PuO2(NO3)2) it was concluded that Pu(III) may have a wide natural occurrence, especially in acidic environments [24].

To assess the sorption behavior of Pu(III), the sorption of Pu(IV) was compared with the similar sorption of Am(III) which can serve as a chemical analogue for Pu(III).

2. Experimental

Triassic clay containing on average 64% of monomontmorillonite, 24% of illite and 12% of chlorite minerals (in the fraction of < 1 μm) was used in this study. In the coating of three clay samples (S, 6 and 7) variable concentration and...
composition of iron oxides was found. These samples were used in previous studies to assess the effect of coating composition on the sorption behavior of radionuclides [25, 26]. The S clay with the most typical composition of iron oxides was employed in this study. Chemical composition and selected physical and chemical properties of the clay sample are presented in Table 1. Synthesis of iron oxides and their characteristics were described earlier [27]. Mössbauer spectroscopy was used to determine iron speciation in the clay and to measure iron oxides leaching during the sequential extraction (using the following extractants: F1 – 0.01 mol/L CH₃COOH, F2 – 0.5 mol/L NH₄OH·HCl, F3: 8.8 mol/L H₂O₂ (1 : 10), then, 1.0 mol/L, CH₃COONH₄ (1 : 50) – oxidizable fraction (bound to organic matter), F₄ – HCl 3 : 1 HNO₃ (1 : 20) – residual fraction (bound to minerals) [28]. ²³⁸Pu was used to monitor plutonium readsorption during the sequential extraction. Readsorption of americium was evaluated in parallel samples using ²⁴¹Am. Details about the physical characteristics of the clay, hematite, goethite and magnetite used in these studies, and about the techniques used for their mineral characterization were previously given [29, 30].

The composition of synthetic rainwater (SRW) was chosen on the basis of long-term observations performed near to the potential site of a planned radwaste repository. SRW, filtered through a 0.45 μm membrane filter, was contacted with a solidified and then crushed locally available Portland cement to obtain the synthetic rainwater – cement water (SRWCW) solution (Table 2). Simulation of the real conditions at the repository requires that ionic strength and concentrations of major cations be varied with the change in pH, contrary to the common studies of pH dependence of sorption, when other parameters than pH are held constant as much as possible. Therefore, cement-rainwater solutions of different dilutions were prepared by mixing SRW with SRWCW solutions characterized in Table 3. The variations of pH, ionic strength and concentrations of Ca, Na, K ion are shown in Fig. 1c. Carbonate was not excluded from the solutions, CO₂ (inorganic carbon) was measured in solutions before experiments using a LECO CS–125 analyzer. In another experiment, sorption was studied using 0.01 or 0.1 mol/L NaNO₃ solutions in MilliQ water with TOC < 10 ppb and under argon atmosphere.

The laboratory batch method described earlier was used for all sorption studies [31]. The method was slightly modified by measuring the pH before and after the sorption experiments as well as by an additional analyses of the Pu oxidation states. The solutions were mixed with weighed amounts of solids in polypropylene bottles at the solid : liquid ratio of 1 : 10 or 1 : 1000 g/mL. The pH of the solutions was adjusted with nitric acid to the desired value and a repeated wash with fresh portions of the working solution was performed until the pH remained stable over the intended range (± 0.1 pH units) for 48 h. Then Pu(IV) – a mixture of ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu and ²⁴¹Am(III) spikes were added to achieve their initial concentrations 1 × 10⁻¹⁰ and 3 × 10⁻¹² mol/L, respectively. The plutonium used was separated from a highly contaminated the Chernobyl soil sample [16, 29] and converted to Pu(IV) form via ion exchange as described by Lovett and Nelson [32]. Oxidation state analysis performed on all spike solutions using TTA extraction [33] showed that typically 96 ± 3% of the plutonium was found in the tetravalent state [29].

After the addition of the tracers, the bottles with the solutions were tightly sealed and shaken for desired time. Then the solids were separated from liquid phase by centrifugation for 20 min at 10 000 G (8000 rpm) in experiments with clay samples, and at 20 000 G (16 000 rpm) in experiments with iron oxides (smaller colloids were probably removed by the repeated wash during the preequilibration of the system). Zänker et al. found very small difference in separation of iron-containing colloids formed by the weathering of phyllite by centrifugation in the region 10 000 G–46 000 G [34].
After centrifugation, the solutions and SE fractions were evaporated and wet ashed using HCl, HClO₄, HNO₃, H₂O₂. Iron was separated by diisoprophyl ether extractions. Plutonium and americium were determined after radiochemical separation using the UTEVA and TRU (Eichrom Industries) and electrodeposition by means of alpha spectrometry [35]. ²⁴²Pu and ²⁴³Am was used as tracers in the separation procedure. Accuracy and precision of the analysis was tested using reference materials IAEA-135, NIST SRM No 4350B and 4357 as well as information from an intercomparison exercise organized by the Risø National Laboratory, Denmark and proficiency tests organized by National Physical Laboratory, UK [36].

Sorption parameters of Am and Pu were determined from three replicates. The adsorption of radionuclides from solutions to the polypropylene bottle walls was determined in the presence of solid phase. After the sorption experiments, the geological material was removed from the bottles, and Pu and Am was desorbed by 6 mol/L HNO₃. The adsorption varied from 0.1 to 1%, and decreased with an increase of contact time. The sorption loss on the walls was taken into account in the calculations.

The interaction of protons and hydroxyl ions with the clay minerals and iron oxides surface was characterized by acid-base titrations. The test solution vessel with clay or iron oxides (0.05–0.1 g), equilibrated with 50 mL of 0.01–0.1 mol/L NaNO₃ under a continuous flow of argon to prevent CO₂ uptake, was immersed in a water bath thermostated at 25.0 ± 0.1 °C. Readings were recorded 10 and 30 min after the addition of the titrant. Drifts in the measured potential were less than 2 mV between the readings after 10 and 30 min. The pH was measured using WTW SenTix 41 or SenTix 81 pH-electrodes and a WTW inoLab Multi Level 1 meter.

In all experiments, ACS reagent grade or higher grade chemicals were used. All solutions were freshly prepared using deionized (Elix, Milipore) or Milli-Q (Millipore Milli-Q Synthesis A-10) water. X-ray diffraction (XRD) analyses were conducted using a D8 (Bruker AXS) X-ray diffractometer. Determination of surface area was performed using nitrogen adsorption (surface area analyzer NOVA 2200).

3. Results and discussions

3.1 Plutonium and americium sorption to clay in the neutral and alkaline pH regions

Sorption experiments with the mixture of SRW and SRWCW and natural clay were undertaken to simulate conditions as close as possible to those at a low or intermediate waste repository when accidental rainwater breakthrough could cause dissolution of the cement resulting in an increase of major ions and pH (from 4.86 to 11.61) (Fig. 1). Results of these sorption experiments are presented in Fig. 1; $K_d$ (in L/g), concentrations of Pu and Am remaining in the solution (L-P, in mol/L) and forms of Pu and Am bonding to the clay (in mol/g). The bonding was studied by SE. It is assumed that each step of the extraction removed certain components from clay coatings (calcite, iron oxides, humic substances) which were identified using Mössbauer spectroscopy, X-ray diffraction, FTIR spectroscopy.

Fig. 1. Effect of pH, ionic strength and initial composition of contact solution on sorption of Pu and Am to S clay. Pu and Am distribution coefficients (–○–, $K_d$) are given in L/g. Pu and Am concentrations (–□–, L-P) remaining in the solution are given in mol/L. Concentration of Pu and Am forms on clay surface determined as removable fractions by sequential extraction is expressed in mol/g and components of clay coatings extracted during the procedure and identified by spectroscopy methods are as follows: –×– F1 – exchangeable and on carbonates CaCO₃ + FeCO₃; –▼– F2 – on Fe(OH)₃, α-FeOOH + FeCO₃; –■– F3 – on organic matter; –△– F4 – residue containing α-Fe₂O₃. Conditions of experiment are shown as variations in ionic strength –○– and in concentration of main ions K⁺ –□–, Ca²⁺ –△–, Na⁺ –×–. Clay concentration used in experiment is $[\text{Clay}] = 2140 \text{ m}^2/\text{L}$ and contact time 10 d.

As shown in Fig. 1, the bonding of Pu and Am to the solids is different: Pu is mainly bound to the iron oxides (F2, F4) while the largest portion of Am is found in exchangeable and carbonate fraction (F1). The amount of Am bound to easily reducible oxides (F2) is twice smaller (30%) than that of Pu and decreases in the high pH region. Similar sorption of both radionuclides on organic matter (F3) has
been observed with a minimum at pH 8–9 and a maximum at pH 10–11. The variations in the sorption patterns of Pu(IV) and Am(III) to components of the clay at the expected conditions of the repository are likely due to changes in aqueous speciation of the elements.

The $K_d$ values obtained for the sorption of Pu on the clay correlate well ($R = 0.85$, $N = 9$) with the Pu amount (mol/g) removed from the clay surface during the second step of SE (fraction F2). During this extraction step, a strong reducing agent was used to dissolve easily reducible iron oxides. Pu sorbed to these oxides was also reduced and released into solution. Typically over 90% of Pu(III) was found in the extracts. The fourth step resulted in the quantitative extraction of hematite. The portion of plutonium released in to solution of this fraction ranged from 30 to 40%.

Our studies of the Pu oxidation state distribution showed that about 10–20% Pu can be bound to this clay as Pu(III), while most of Pu is sorbed in tetravalent form and can be released into solution as Pu(IV) and/or a Pu(IV-polymeric) form during the leaching, depending on HCl concentration used [20, 21]. Leaching of iron hydroxides (Fe(OH)$_3$), goethite ($\alpha$-FeOOH), siderite (FeCO$_3$) and hematite ($\alpha$-Fe$_2$O$_3$) from the clay was checked by means of Mössbauer spectroscopy after each step of the SE procedure [29]. It was found that the first step of the extraction removed mainly CaCO$_3$, whereas only a small amount of siderite was extracted. The presence of CaCO$_3$ in the clay was identified using X-ray diffraction analyses. Mn oxides were below the detection limit of this method. The approximately equal amounts of Mn leached during steps F1–F4 (determined by atomic absorption spectrometry) suggested that Mn was present in the clay coating and that Mn oxides did not play a dominant role in the sorption [30].

Na$^+$, K$^+$ and Ca$^{2+}$ cations released from cements and concrete by percolating water probably do not compete for the sorption sites with actinides due to their different chemistry [8]. However, stabilization of plutonium and americium in solution by formation of their carbonate complexes can be one of the reasons of the slight decrease of their sorption on clay at pH > 8. Another reason can be complexation of the actinides by organic substances released from the clay into alkaline solutions. Such release was observed by Claret et al. [37] in experiments with clay containing low amounts of organics (TOC 1.3 wt %). The authors concluded that the humics can affect solubility of radionuclides at high pH values that are characteristic of a cement-based repository. Similar effect of humic substances was shown in studies with Eu(III) [38]. The authors observed a decrease in the uptake of Eu(III) by attapulgite at pH 4–8 in the presence of humic and fulvic acids and explained it via Eu$^{3+}$ complexation in solution. Recently, it has been shown that humic and fulvic acids present in groundwater can stabilize small Pu(IV) hydrolysis species and inhibit precipitation of polynuclear hydrolysis products [39].

In spite of the low content of TOC, the presence of organic substances on the surface of our clay particles was proven by FTIR spectroscopy. Our preliminary data suggest that they are mostly humic and/or fulvic substances (a more exact identification is in progress) and can affect sorption of Pu(IV) and Am to clay particles [Lujaniene et al., unpublished results]. An increase in association of Am in the residual fraction at pH 11.6 (Fig. 1b) can probably be explained by Am incorporation to clay minerals. A similar but more pronounced increase (up to 20%) was observed at pH 12.6 (Lujaniene, unpublished results) in analogous experiments with groundwater – cement water. Studies of Am(III), Eu(III) and Cm(III) interaction with calcite showed that the Ca$^{2+}$ can be replaced by Eu$^{3+}$ and that Cm(III) initially sorbed at the calcite surface, forming a partially hydrated Cm(III) species with one H$_2$O molecule in the first coordination sphere, while with increasing contact time Cm(III) was incorporated into the calcite. The investigation of Am(III) and Cm(III) incorporation mechanism into calcite by time-resolved laser fluorescence spectroscopy showed two different Am(III)/Cm(III)/calcite species – one bonded onto the calcite surface and the second one incorporated into the calcite bulk structure [40–42].

Association of Am with iron oxides (fraction 2) can be explained by sorption to ferrihydrite. This is supported by data obtained using EXAFS which showed the formation of a bidentate corner-sharing Am(III) species on the surface at pH 5.5 and 8 [43].

### 3.2 Experimental sorption studies and modeling

The sorption of Pu(IV) and Am(III) to natural clay S of complex composition and to synthetic minerals can represent phases of the coatings in this mineral (goethite, hematite and magnetite) that can form under anoxic conditions. The selected materials were studied as a function of pH in NaNO$_3$ solutions and, in the case of S-clay, also for two ionic strengths. The used ionic strength range corresponded to the sorption experiments with SRWCW. The use of nitrate solution is representative of many types of radioactive waste which contain high concentrations of NO$_3^-$ ions (e.g., evaporated concentrate).

The sorption was modeled using a surface complexation model (SCM) assuming reactions on the so-called “edge sites” and an ion exchange model (IExM) for ion exchange on the so called “layer sites”. These two kinds of sorption sites are commonly used in modeling the sorption on clay minerals [44, 45]. In order to enable a comparison of the results for clay and models of its coatings and to facilitate interpretation of sorption at low pH values, the existence of the “layer sites” was assumed also for iron oxide minerals having different structure than the clay. The usefulness of such an approach has been demonstrated in a previous study [45], where a more detailed discussion is given.

The choice of sorption reactions for the models was based on the speciation of Pu and Am in the sorption solutions (see Fig. 2), calculated using an own speciation code (PuAmSpec.fm) and stability constants shown in Table 3. The following reactions were considered:

- **reactions on edge sites (SOH$^0$, SO$^-$, SOH$_2^+$)**
  - $\text{SO}^- + \text{H}^+ \leftrightarrow \text{SOH}^0$ \hspace{1cm} KS1
  - $\text{SOH}^0 + \text{H}^+ \leftrightarrow \text{SOH}_2^+$ \hspace{1cm} KS2
  - $\text{SO}^- + \text{Pu(OH)}_3^- \leftrightarrow \text{SOPu(OH)}_2^-$ \hspace{1cm} K1
  - $\text{SO}^- + \text{Am(OH)}^{2+} \leftrightarrow \text{SOAm(OH)}^+$ \hspace{1cm} K2
  - $\text{SO}^- + \text{Am(OH)}^{2+} \leftrightarrow \text{SOAm(OH)}_2^0$ \hspace{1cm} K3
  - $(\text{SOH}_2^+ + \text{NO}_3^- \leftrightarrow \text{SOH}_2\text{NO}_3^0)$
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Fig. 2. Data on the sorption of Pu(IV) and Am(III) (%) on clay S fitted with sorption models and compared with calculated speciation of Am and Pu in 0.1 mol/L NaNO$_3$ and on the clay. [Clay] = 1 g/L.

Three types of SCMs, namely two electrostatic, i.e., the constant capacitance (CCM) and the diffuse double layer (DLM) model, and one chemical equilibrium non-electrostatic model (CEM), were employed to simulate first the amphoteric and then the sorption properties of the minerals. From the evaluation of acid base titration curves, the protonation constants (KS1, KS2 – characterizing “edge sites”), ion-exchange constant (KX – characterizing the “layer sites”) and the total concentrations of both edge and layer sites (ΣSOH, ΣXH) were obtained. Then the values of equilibrium constants (K1–K6) were sought by means of the Newton-Raphson multidimensional nonlinear regression method. The best fit was found if the experimental data were fitted with the non-electrostatic model (CEM). The respective computational codes, PuAmSor2.fm and PuAmSor3.fm (Program Package Stamb-2009), were constructed using the software product FAMULUS.

The fitting proceeded in the iteration cycle, from which it was possible to determine the sought parameters when the difference of the sum of relative squares of deviations (SSx), after two successive cycles (i.e. $i^{th}$ and $i^{th+1}$), was less than $10^{-8}$ – see Eq. (1)

$$SSx_i = \Sigma((C_{cal} - C_{exp})_i/(C_{exp})_i)^2$$

As a fitting criterion, reflecting the agreement between calculated and experimental values, the WSOS/DF (Weighted Sum of Squares divided by the Degrees of Freedom) quantity was used as defined in [46]. Generally, the agreement is acceptable if $0.1 \leq$ WSOS/DF $\leq 20$.

The input data for the codes mentioned above, namely, the values of constants KS1, KS2 and KX and of quantities ΣSOH, ΣXH, can be found in Table 4. The resulting values of equilibrium constants and of parameter WSOS/DF are summarized in Table 5. According to the values of the fitting criterion WSOS/DF, agreement between the calculated and experimental sorption values seems to be very good. WSOS/DF is slightly outside the interval of the recommended values (see above) only in the case of magnetite.

The values of the constants and total concentrations of the edge and layer sites presented in Table 4 reflect the surface properties of the minerals used in our study. For all samples studied, the pH of point of zero charge (pH$_{pzc}$) was determined using acid base titration data. The variations in pH$_{pzc}$ are known to be dependent on the method of their determination, on sample composition (admixtures), structure and pre-treatment, on temperature and ionic strength. The obtained data are within the range of those published in the literature [44]. pH$_{pzc}$ of magnetite significantly differs from the same parameter of the other minerals. The total concen-
tration of edge sites of hematite is relatively high, whereas for the other minerals it is lower, approximately at the bentonite level. A similar analogy holds in case of total concentrations of layer sites: for S clay, hematite and magnetite, they are approximately at the bentonite level, for goethite it is higher by approximately 0.5–1 order of magnitude.

An example of the modeling results is shown in the Fig. 2. The importance of individual sorption mechanisms is characterized in Table 5 by comparison of the corresponding reaction constants. It was found that not all reaction equilibria listed above play an important role in modeling the sorption. This applies particularly for the constants characterizing the sorption on layer sites: comparison of K4 values with those for K5 and K6 indicates that Pu(IV) is sorbed more than Am(III) on all the minerals studied. This effect is most pronounced for S clay and magnetite. The comparison of constants K5 and K6 is very interesting because it points to the great difference between the affinity of layer sites for Am(III) and AmNO32+, which is much higher for AmNO32+.

Data from sequential extraction presented in Fig. 1 indicated the importance of iron oxides for the sorption of Pu(IV), but not of Am(III), on the clay samples studied, which is in good agreement with the published data for other systems. Modeling of the sorption using the so-called generalized composite approach provided valuable information about possible sorption mechanisms. However, comparison of the stability constants obtained by the modeling (Table 5) does not confirm the conclusions derived from sequential extraction as the sorption affinity of the clay for Pu is higher than that of the iron oxides studied, while the sorption affinities for Am are mutually comparable. This discrepancy suggests that for better characterization of the role of surface coatings in radionuclide sorption on clay minerals. More detailed analyses of the coatings should be made, including the study of the formation of secondary minerals in contact with the solution. This can be aided by surface complexation modeling, preferably using the so-called component additivity approach. Comparison of the constants for Pu (K4) and Am (K5,6) exchange on the layer sites presented in Table 3 indicates that Pu is much more selectively (i.e., strongly) bound by this mechanism than Am on all the minerals studied. This is important for understanding sorption behavior of Am(III) and Pu(III) in the environment. The results correspond well with the higher exchangeability of Am found by SE and can explain the higher Am mobility in the environment when compared to Pu.

4. Conclusions

Experimental results indicated that infiltration of rain water and dissolution of cement in solidified radioactive waste can cause wide variations in the binding patterns of Pu(IV) and Am(III) on natural clay. Data of sequential extraction (SE) showed that Pu(IV) was stronger bound to the clay than Am(III) which was mostly found in exchangeable and car-

Table 4. Input data for the codes PuAmSor2.fm and PuAmSor3.fm (I = 0) and values of point of zero charge pH (pH_pzc = (log K1 + log K2)/2).

| Mineral | KS1 (L/mol) | KS2 (L/mol) | ΣSOH (mol/kg) | KX | ΣXH (mol/kg) | pH_pzc | WSOS/DF |
|---------|-------------|-------------|--------------|----|-------------|--------|---------|
| S Clay  | 3.80 × 10^{-9} | 3.88 × 10^{-3} | 9.30 × 10^{-2} | 1.62 × 10^{-6} | 2.74 × 10^{-2} | 6.58 | 1.29 |
| Goethite | 1.13 × 10^{-11} | 1.71 × 10^{-2} | 2.49 × 10^{-9} | 1.60 × 10^{-5} | 5.64 × 10^{-2} | 6.64 | 0.50 |
| Magnetite | 1.85 × 10^{-7} | 1.32 × 10^{-2} | 1.50 × 10^{-1} | 3.48 × 10^{-4} | 4.59 × 10^{-2} | 5.69 | 0.88 |

Table 5. Values of equilibrium constants (I = 0) and of the quantity WSOS/DF (pH regions where the constants are important are shown in brackets).

| Mineral | K1 SOPu(OH)4− (L/mol) | K2 SOAm(OH)3+ (L/mol) | K3 SOAm(OH)2− (L/mol) | K4 XPu(OH)3− | K5 X3Am | K6 X2AmNO3 (kg/L) | WSOS/DF |
|---------|----------------------|-----------------------|-----------------------|--------------|--------|-------------------|---------|
| S Clay  | 7.00 × 10^{-7} (pH > 5) | 4.03 × 10^{-11} (pH > 9) | 1.51 × 10^{-13} (pH > 7) | 4.40 × 10^{-10} (pH > 8) | 2.33 × 10^{-8} (pH > 5) | 2.05 × 10^{-11} (pH < 8) | 0.50 |
| Goethite | 1.89 × 10^{-7} (pH > 7) | 1.32 × 10^{-12} (pH > 8) | 5.60 × 10^{-12} (pH > 6) | 6.02 × 10^{-7} (pH > 5) | 5.68 × 10^{-5} (pH > 6) | 1.83 × 10^{-1} (pH < 6) | 1.40 |
| Magnetite | 6.28 × 10^{-7} (pH > 8) | 2.57 × 10^{-11} (pH > 7) | 9.44 × 10^{-10} (pH > 6) | 7.97 × 10^{-10} (pH > 6) | 1.50 × 10^{-7} (pH > 5) | 4.77 × 10^{-4} (pH > 5) | 18.06 |

a: Corresponding reactions play minimal role; b: NaNO3 solutions used in experiments.
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bonate fraction of SE. This is in a good agreement with modeling results indicating that Pu(IV) is more strongly sorbed than Am(III) on all minerals studied, and especially on S clay and magnetite. In contrast to the sequential extraction data on prevailing Pu(IV) association with iron oxides, the stability constants obtained by the modeling (Table 5) indicated higher sorption of Pu(IV) to clay than to iron oxides, whereas the sorption affinities of these minerals for Am are mutually comparable. Thus, a more accurate characterization of clay coatings is required and should include the analysis of possible transformations of the coatings components. Effects of components present in very small amounts such as organic substances and Mn oxides should also be studied.

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