



Modeling plutonium sorption to kaolinite: Accounting for redox equilibria and the stability of surface species



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ABSTRACT

Plutonium with its particularly complex redox chemistry may be thermodynamically stable in the states +III to +VI depending on the redox conditions in the environment. Mineral surfaces can also affect Pu redox speciation. Therefore, the interpretation of Pu sorption data becomes particularly challenging, even for simplified laboratory experiments. The present study focuses on Pu sorption to kaolinite. Am(III), Th(IV), Np(V) and U(VI) literature sorption data are used as analogues for the corresponding Pu redox states to calibrate a simple surface complexation model, and the Nernst formalism is applied. Two independent pH–pe diagrams, one for the kaolinite surface and another for the aqueous phase, are constructed and superimposed. This allows visualization of the prevalent Pu redox state in both phases. The model suggests that the stability field of the most strongly adsorbing redox state is larger at the surface than in solution. Because Pu(V) weakly sorbs to kaolinite, it never prevails at the surface. Within the stability field of Pu(V) in 0.1 M NaClO₄ solution, Pu(VI) and Pu(IV) prevail at the kaolinite surface under oxidizing and slightly reducing conditions, respectively. By contrast, the Pu(IV)/Pu(III) boundary is hardly affected because both redox states strongly sorb to kaolinite, especially for pH > 6. The present method is applied to literature data for Pu sorption to kaolinite. By estimating the pe from a Pu redox state analysis in solution, overall Pu uptake could be predicted. Generic equations are derived that are applicable to minerals and actinides other than kaolinite and Pu. The present study provides important progress in understanding Pu geochemistry, especially in the context of nuclear waste disposal where thermodynamic models are particularly necessary to predict Pu mobility.

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1. Introduction

Due to its radiotoxicity and the very long half-lives of several isotopes, plutonium (Pu) is an important element in the context of nuclear waste disposal as well as in remediation of areas contaminated by nuclear weapon testing or nuclear power-plant accidents. Geochemical behavior of Pu is particularly challenging since, in environmentally relevant conditions, Pu can be found in the oxidation states +III, +IV, +V or +VI. Pu(III) or Pu(IV) prevail under reducing conditions, which are particularly relevant for deep geological nuclear waste disposal. Pu(V) or Pu(VI) are more relevant under oxidizing conditions like oxygenated surface environments. The chemical behavior of Pu concerning complexation by organic and inorganic ligands, solubility, as well as sorption to minerals, strongly depends on the Pu redox state (e.g. Altmaier et al., 2013). Thus, Pu(V) weakly sorbs to minerals and is considered to be rather mobile (e.g. Geckeis et al., 2013). Pu(VI) and Pu(III) sorption is pH dependent and can be affected by the presence of carbonates (especially for Pu(VI)). Pu(IV) strongly sorbs to minerals, is sparingly soluble and,

therefore, considered to be rather immobile. However, Pu(IV) also tends to form intrinsic colloids in neutral to alkaline conditions, which might enhance its mobility (Neck et al., 2007; Kersting, 2013; Walther and Denecke, 2013). Consequently, sound knowledge of the geochemical behavior of each Pu redox state is required to understand and predict Pu mobility in the environment. In this context, the development of geochemical models that predict Pu speciation accounting for all these processes are required.

Sorption to mineral surfaces can retard Pu migration or mediate its migration when Pu sorbs to mineral colloids (Kersting et al., 1999; Xie et al., 2013), if these colloids remain stable in aqueous suspension and can be transported by water flow. Because of the complexity of the mineral–water interface and of the heterogeneity of minerals in nature, laboratory studies with purified or synthetic minerals are carried out to unravel the underlying processes. Even though such simplified systems have been widely investigated, the chemical behavior of Pu still remains unclear. In particular, although introduced in a single redox state to a mineral suspension, a mixture of Pu redox states rapidly emerges. For instance, when added either as Pu(VI) or Pu(V) under ambient (air) atmosphere, Pu(V) prevails in solution at the end of the experiment, but Pu(IV) is found at the surface of hematite, goethite, magnetite

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(Powell et al., 2004; 2005; Romanchuk et al., 2011; 2013; Hixon and Powell, 2014), quartz/silica (Kumar et al., 2012; Hixon et al., 2013) or montmorillonite (Zavarin et al., 2012). Similar observations were recently made in the case of neptunium (Np) interaction with illite (Marsac et al., 2015). Although initially introduced as Np(V) under oxygen-free argon atmosphere, a significant amount of Np(IV) was found at the surface, whereas a small fraction remained in solution as Np(V). Conversely, when Pu(IV) was added either under argon or ambient atmosphere, Pu(V) was found in solution in the presence of kaolinite (Banik et al., 2007). Pu(III) sorption to minerals has been probed less frequently, although it has high environmental relevance (Kaplan et al., 2007; Lujanienė et al., 2009; Kirsch et al., 2011). Buda et al. (2008) reacted Pu(III) with kaolinite in the presence of $\text{NH}_2\text{OH}\cdot\text{HCl}$ as reducing agent. A preliminary experiment, in the absence of kaolinite, showed that Pu(III) was not stable and Pu(IV) formed in solution in the presence of $\text{NH}_2\text{OH}\cdot\text{HCl}$ for $\text{pH} > 6$. In the presence of kaolinite, the pH-edges of Pu and Am(III) were found to be very similar, the sorption plateau being reached for $\text{pH} \approx 6$. This suggests that the Pu(IV)/Pu(III) redox couple is only weakly affected by sorption.

It appears from all these studies that mineral surfaces have a strong impact on Pu redox speciation, especially when the Pu(V)/Pu(IV) couple is involved. Furthermore, these studies also show that the prevalent redox state of the metal ion in aqueous solution can differ from that at the mineral surface. In principle, the overall redox potential of the system should determine the final redox state of Pu (Geckeis et al., 2013). It has been previously proposed that the strongly adsorbing Pu(IV) is thermodynamically favored at a mineral surface compared to Pu(V) (Hixon et al., 2013; Hixon and Powell, 2014). With such an approach, the Np sorption to illite and redox speciation could recently be described in a quantitative way considering Np(IV) at the mineral surface and Np(V) in solution (Marsac et al., 2015). This approach might also be suitable in the case of Pu, because of the very similar chemistry of both actinides.

To determine the stability fields of different Pu redox states at a mineral surface, the sorption behavior of all redox states must be known separately. It appears that for Pu such experimental data will hardly ever become available because a mixture of redox states is found in most experimental studies. Fortunately, lanthanides/actinides (Ln/An) exhibit similar chemical behavior for the same redox state, even though thermodynamic constants may significantly differ between two elements (Altmaier et al., 2013). The use of these elements as chemical analogues might help to unravel the complex geochemical behavior of Pu in a first approach (Choppin, 1999).

The present study focuses on kaolinite because experimental sorption data for americium(III) (Am^{3+}), thorium(IV) (Th^{4+}), neptunium(V) (NpO_2^+) and uranium(VI) (UO_2^{2+}) are available (Banik et al., 2007; Křepelová, 2007; Buda et al., 2008; Amayri et al., 2011). These data are assumed to be representative for sorption of Pu(III, IV, V, VI), respectively, and used for each redox state of Pu to calibrate the simple surface complexation model developed by Tertre et al. (2008). By merging Pu redox chemistry with sorption processes, the resulting model is used to construct a predominance (pH–pe) diagram for Pu redox speciation at the kaolinite surface. The modeling results are compared with experimental data in order to test the capacity of the model to predict Pu sorption to kaolinite as a function of pH and pe. The present approach is subsequently tested on metal sorption on other minerals.

2. Materials and method

2.1. Geochemical speciation code and thermodynamic database

PHREEQC (version 2; Parkhurst and Appelo, 1999) is a computer code that can perform speciation (including surface complexation) and saturation-index calculations in water. Predominance (pH–pe) diagrams can be obtained using PhreePlot (Kinniburgh and Cooper,

2009), which contains an embedded version of PHREEQC. In the present work, thermodynamic constants for Pu aqueous speciation and solubility are taken from the NEA thermodynamic database (Guillaumont et al., 2003). Reactions and corresponding thermodynamic constants at 25 °C and zero ionic strength are given in Table 1. In case of gaps in the Pu database, data for analogues were chosen and are included in Table 1. A redox reaction involving aqueous Pu^{4+} and PuO_2^+ is not given. It is calculated based on the reaction $\text{PuO}_2(\text{am,hyd}) = \text{PuO}_2^+ + \text{e}^-$ with $\log K = -19.78$ at zero ionic strength (Guillaumont et al., 2003). The specific ion interaction theory (SIT; Ciavatta, 1980) accounts for ionic strength effects and the corresponding parameters for Pu (or the chosen analogue) from Guillaumont et al. (2003) are used.

2.2. Surface complexation modeling

As for other clay minerals, the kaolinite surface is complex because of the presence of various types of hydroxyl surface groups, mainly silanols (SiOH) and aluminols (AlOH), that can bind cations. Furthermore, several faces with different charging properties occur (Miller et al., 2007) making the development of mechanistic models a challenging task. Tertre et al. (2008) showed that batch uptake data

Table 1

Thermodynamic constants at zero ionic strength used in the present study (Guillaumont et al., 2003). The missing hydrolysis constants for Pu are taken from the corresponding analogues (in brackets). Surface complexation constants for Pu(III, IV, V, VI) are obtained assuming that the experimental uptake data of Am(III), Th(IV), Np(V) and U(VI) by kaolinite are representative for the uptake of the corresponding Pu redox states. (*) Exchange and surface complexation constants have been determined by Tertre et al. (2008). Some constants could not be determined since no appropriate experimental data were available. According to Tertre et al. (2006, 2008), the surface area of kaolinite is $10 \text{ m}^2/\text{g}$, site density for SiOH and exchange sites are 1.66 and $3.70 \text{ } \mu\text{mol}/\text{m}^2$, respectively.

| | Reaction | Log K (I = 0) |
|---|--|------------------|
| Solubility Redox | $\text{PuO}_2(\text{am,hyd}) + 2 \text{H}_2\text{O} = \text{Pu}^{4+} + 4 \text{OH}^-$ | −58.33 |
| | $\text{PuO}_2^+ + \text{e}^- = \text{PuO}_2^+$ | 15.82 |
| | $\text{PuO}_2^+ + 4 \text{H}^+ + 2 \text{e}^- = \text{Pu}^{4+} + 2 \text{H}_2\text{O}$ | 33.27 |
| | $\text{PuO}_2^+ + 4 \text{H}^+ + \text{e}^- = \text{Pu}^{4+} + 2 \text{H}_2\text{O}$ | 17.45 |
| | $\text{Pu}^{4+} + \text{e}^- = \text{Pu}^{3+}$ | 17.69 |
| Hydrolysis | $\text{PuO}_2^+ + \text{H}_2\text{O} = \text{PuO}_2\text{OH}^+ + \text{H}^+$ | −5.50 |
| | $\text{PuO}_2^+ + 2 \text{H}_2\text{O} = \text{PuO}_2(\text{OH})_2 + 2 \text{H}^+$ | −13.20 |
| | $\text{PuO}_2^+ + 3 \text{H}_2\text{O} = \text{PuO}_2(\text{OH})_3^- + 3 \text{H}^+$ | −20.25 (U) |
| | $\text{PuO}_2^+ + 4 \text{H}_2\text{O} = \text{PuO}_2(\text{OH})_4^{2-} + 4 \text{H}^+$ | −32.40 (U) |
| | $\text{PuO}_2^+ + \text{H}_2\text{O} = \text{PuO}_2\text{OH} + \text{H}^+$ | −11.30 (Np) |
| | $\text{PuO}_2^+ + 2 \text{H}_2\text{O} = \text{PuO}_2(\text{OH})_2^+ + 2 \text{H}^+$ | −23.60 (Np) |
| | $\text{Pu}^{4+} + \text{H}_2\text{O} = \text{PuOH}^{3+} + \text{H}^+$ | 0.60 |
| | $\text{Pu}^{4+} + 2 \text{H}_2\text{O} = \text{Pu}(\text{OH})_2^{2+} + 2 \text{H}^+$ | 0.60 |
| | $\text{Pu}^{4+} + 3 \text{H}_2\text{O} = \text{Pu}(\text{OH})_3^+ + 3 \text{H}^+$ | −2.30 |
| | $\text{Pu}^{4+} + 4 \text{H}_2\text{O} = \text{Pu}(\text{OH})_4 + 4 \text{H}^+$ | −8.50 |
| | $\text{Pu}^{3+} + \text{H}_2\text{O} = \text{PuOH}^{2+} + \text{H}^+$ | −6.90 |
| $\text{Pu}^{3+} + 2 \text{H}_2\text{O} = \text{Pu}(\text{OH})_2^+ + 2 \text{H}^+$ | −15.10 (Am) | |
| $\text{Pu}^{3+} + 3 \text{H}_2\text{O} = \text{Pu}(\text{OH})_3 + 3 \text{H}^+$ | −26.20 (Am) | |
| Exchange | $2 \text{X-Na} + \text{PuO}_2^+ = \text{X}_2\text{-PuO}_2 + \text{Na}^+$ | nd |
| | $\text{X-Na} + \text{PuO}_2^+ = \text{X-PuO}_2 + \text{Na}^+$ | nd |
| | $3 \text{X-Na} + \text{Pu}^{3+} = \text{X}_3\text{-Pu} + \text{Na}^+$ | 1 |
| | $4 \text{X-Na} + \text{Pu}^{4+} = \text{X}_4\text{-Pu} + \text{Na}^+$ | nd |
| | $\text{X-Na} + \text{H}^+ = \text{X-H} + \text{Na}^+$ | −1(*) |
| | | |
| Surface complexation | $\text{SiOH} + \text{PuO}_2^+ = \text{SiO-PuO}_2^+ + \text{H}^+$ | 0.2 |
| | $\text{SiOH} + \text{PuO}_2^+ + \text{H}_2\text{O} = \text{SiO-PuO}_2\text{OH} + \text{H}^+$ | −6.9 |
| | $\text{SiOH} + \text{PuO}_2^+ + 2 \text{H}_2\text{O} = \text{SiO-PuO}_2(\text{OH})_2^- + 3 \text{H}^+$ | −14.5 |
| | $\text{SiOH} + \text{PuO}_2^+ = \text{SiO-PuO}_2 + \text{H}^+$ | −4.0 |
| | $\text{SiOH} + \text{Pu}^{4+} = \text{SiO-Pu}^{3+} + \text{H}^+$ | nd |
| | $\text{SiOH} + \text{Pu}^{4+} + \text{H}_2\text{O} = \text{SiO-PuOH}^{2+} + 2 \text{H}^+$ | 6.0 |
| | $\text{SiOH} + \text{Pu}^{4+} + 2 \text{H}_2\text{O} = \text{SiO-Pu}(\text{OH})_2^+ + 3 \text{H}^+$ | 3.2 |
| | $\text{SiOH} + \text{Pu}^{4+} + 3 \text{H}_2\text{O} = \text{SiO-Pu}(\text{OH})_3 + 4 \text{H}^+$ | −3.0 |
| | $\text{SiOH} + \text{Pu}^{3+} = \text{SiO-Pu}^{2+} + \text{H}^+$ | −0.5(*) (Eu) |
| | $\text{SiOH} + \text{Pu}^{3+} + \text{H}_2\text{O} = \text{SiO-PuOH}^+ + 2 \text{H}^+$ | −9.3 |

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