



# Dissolution of uranyl and plutonyl borates: Influences of crystalline structures and aqueous ligands

Yu Yang<sup>a,b,1</sup>, Shuao Wang<sup>a,b,2</sup>, Matthew J. Polinski<sup>a,b</sup>, Yi Liu<sup>a,b</sup>,  
Mark O. Barnett<sup>c</sup>, Thomas E. Albrecht-Schmitt<sup>d,\*</sup>

<sup>a</sup> Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick Hall, South Bend, IN 46556, USA

<sup>b</sup> Department of Chemistry and Biochemistry, University of Notre Dame, 156 Fitzpatrick Hall, South Bend, IN 46556, USA

<sup>c</sup> Department of Civil Engineering, 238 Harbert Engineering Center, Auburn University, Auburn, AL 36849, USA

<sup>d</sup> Department of Chemistry and Biochemistry, Florida State University, 95 Chieftan Way, 310 DLC, Tallahassee, FL 32306-4390, USA

## ARTICLE INFO

### Article history:

Received 15 January 2013

Received in revised form 14 August 2013

Accepted 19 August 2013

Available online 28 August 2013

Editor: J. Fein

### Keywords:

Uranyl borate

Plutonyl borate

Crystal dissolution

Aqueous ligands

## ABSTRACT

Novel crystalline actinide materials can be used to immobilize uranium and transuranium elements at radioactive waste disposal sites. However, the stability and dissolution of such phases are still poorly understood. In this study, we investigated the dissolution kinetics of two uranyl borates and one plutonyl borate,  $\text{UO}_2\text{B}_2\text{O}_4$  (UBO),  $\text{Na}[(\text{UO}_2)\text{B}_6\text{O}_{10}(\text{OH})]\cdot 2\text{H}_2\text{O}$  (NaUBO), and  $\text{PuO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]$  (PuBO), with three different ligands, i.e., bicarbonate, phosphate, and natural humic acid (HA). These actinide borates were chosen because they possess different topologies that may influence dissolution. In the presence of bicarbonate, the apparent steady-state concentration of dissolved U(VI) and surface area-normalized dissolution rates were much higher for UBO compared to NaUBO. Uranyl phosphate, most likely in the form of  $(\text{UO}_2)_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$ , was precipitated on the surface of residual particles of UBO and NaUBO with phosphate. The dissolution rate of PuBO in  $\text{NaNO}_3$  solution was much higher than UBO or NaUBO. This study revealed that actinide borate crystal dissolution was substantially influenced by crystalline structures of actinide borates and aqueous ligands.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Sustainable development of nuclear energy requires appropriate disposal of nuclear waste and efficient remediation of radionuclide contamination (Grambow, 2006; Yasunari et al., 2011). As a remediation strategy, novel crystalline actinide materials have been synthesized for immobilizing radionuclides from liquid waste (Wu et al., 2010; Wang et al., 2011a, 2011b, 2011c, 2011d; Wu et al., 2011). Nanoscale uranyl clusters were produced with potential applications in separating actinides from radioactive waste (Burns, 2011; Sigmon and Burns, 2011). Wu et al. (2010) demonstrated that  $\text{IO}_3^-$  and  $\text{NpO}_2^+$  can be simultaneously incorporated into  $\text{Ba}_3(\text{UO}_2)_2(\text{HPO}_4)_2(\text{PO}_4)_2$ , by substitution of  $\text{NpO}_2^+ \leftrightarrow \text{UO}_2^{2+}$  and  $\text{IO}_3^- \leftrightarrow \text{HPO}_4^{2-}$ . Recently, Wang et al. (2010a, 2010b, 2010c, 2010d, 2011a, 2011b) used boric acid as a reactive flux to produce a large family of actinide borates and demonstrated that some of these materials have substantial incorporation capacity for transuranium radionuclides.

Successful application of actinide solids to sequester radionuclides greatly depends on the stability of these materials in the natural environment, as actinide crystals may be degraded or dissolved through interactions with aqueous ligands (Selvig et al., 2005; Gorman-Lewis et al., 2008a, 2008b; Schindler et al., 2009). Because of the complexation between uranyl cations and carbonate, the concentration of carbonate/bicarbonate in solution can substantially influence the dissolution rate and solubility of uranium solids (e.g., uranium phosphate deposits and uranium silicate micro precipitates) (Liu et al., 2004; Shlewit and Alibrahim, 2008). Phosphate can induce the dissolution of actinides by surface complexation, while the formation of phosphate precipitates would inhibit dissolution of crystals (Kaplan and Knox, 2004; Ilton et al., 2010; Singh et al., 2010). The sorption of phosphate on the crystal surface can also influence the dissolution of uranyl compounds and fate of uranium in the aqueous environment (Cheng et al., 2004; Singh et al., 2010). In addition, the presence and concentration of organic ligands, e.g. citric acid, tris(hydroxymethyl)aminomethane (TRIS), and ethylenediaminetetraacetate (EDTA), also greatly influenced the kinetics and thermodynamics for the dissolution of actinide minerals (Wellman et al., 2006; Luo and Gu, 2011). Natural organic matter, such as humic acid (HA), widely exists in the environment and can associate with actinides through complex interactions (Kim and Czerwinski, 1996; De Stefano et al., 2011).

\* Corresponding author. Tel.: +1 850 645 0477.

E-mail address: [albrecht-schmitt@chem.fsu.edu](mailto:albrecht-schmitt@chem.fsu.edu) (T.E. Albrecht-Schmitt).

<sup>1</sup> Current address: Department of Chemical and Environmental Engineering, Yale University, 9 Hillhouse Avenue, New Haven, CT 06511, USA.

<sup>2</sup> Current address: Department of Chemistry, University of California, Berkeley, 70A1150, Berkeley, CA 94720, USA.

In addition to aqueous ligands, crystalline structures of radionuclide compounds play an important role in governing their solubilities and dissolution rates (Gorman-Lewis et al., 2008a, 2009). However, there are limited studies on the dissolution of radionuclide crystals with similar chemical compositions but dissimilar crystalline structures, which can provide deep insight into how the crystalline structures of radioactive compounds alter their dissolution. Furthermore, uranium compounds have often been used as surrogates for transuranium compounds, while the differences in the dissolutions between transuranium compounds and their analogs have not been thoroughly investigated (Divu et al., 2010a, 2010b).

In this study, we analyzed the dissolution of two uranyl borates and one plutonium borate, i.e.,  $\text{UO}_2\text{B}_2\text{O}_4$  (UBO),  $\text{Na}[(\text{UO}_2)_2\text{B}_6\text{O}_{10}(\text{OH})] \cdot 2\text{H}_2\text{O}$  (NaUBO) and  $\text{PuO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]$  (PuBO) (Wang et al., 2010c, 2010d, 2011b). The different crystalline structures of UBO, NaUBO, and PuBO make them appropriate probes for studying the impact of crystalline structures on the dissolution of actinide compounds. Actinide borates can be used as storage forms for concentrated radionuclide wastes. In addition, borate phases of actinides are likely to exist at radioactive waste disposal sites, when the borate concentration in surrounding geologic media, e.g. the brine salt deposition near Waste Isolation Pilot Plant (WIPP), is relatively high (Wang et al., 2010c, 2010d, 2011b). Investigations of the dissolution of UBO, NaUBO, and PuBO have substantial implications for both facilitating the safe storage of radioactive wastes and uncovering the environmental fate of actinide compounds in polluted sites. The influences of different aqueous ligands, i.e. bicarbonate, phosphate, and natural HAs, on the dissolution kinetics of UBO, NaUBO, and PuBO were analyzed.

## 2. Materials and methods

### 2.1. Synthesis

UBO, NaUBO, and PuBO were synthesized following the previously established methods (Wang et al., 2010c, 2010d, 2011b).  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98%, International Bio-Analytical Industries), boric acid (99.99%, Alfa-Aesar) and  $\text{NaNO}_3$  (99.3%, Fisher) were used as received. Weapons-grade plutonium (94%  $^{239}\text{Pu}$  and 6%  $^{240}\text{Pu}$ ) was used in this study.  $^{239}\text{Pu}$  ( $t_{1/2} = 24,065$  y) and  $^{240}\text{Pu}$  ( $t_{1/2} = 6537$  y) represent serious health risks owing to their  $\alpha$  and  $\gamma$  emissions. All studies with plutonium were conducted in a laboratory dedicated to studies on transuranium elements. A series of counters continually monitor radiation levels in the laboratory. The laboratory is licensed by the Nuclear Regulatory Commission. All experiments were carried out with approved safety operating procedures. Millipore water with resistance of 18.2  $\text{M}\Omega \cdot \text{cm}$  was used in all reactions.

HAs were extracted from a peat soil with 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$  and precipitated by adjusting pH to 1 with concentrated HCl (Yang et al., 2011). The precipitated HA was de-ashed by HCl/HF (0.1/0.3 M) solution for five times, followed by rinsing five times with Millipore water (Yang et al., 2011). The stock HA solution was made by dissolving 0.1 g of de-ashed HA in 2 mL of 0.5 M NaOH and filtering through 2.7  $\mu\text{m}$  membranes (Millipore, Billerica, MA, USA). Organic carbon concentration of HA solution was measured by a total organic carbon (TOC) analyzer (TOC-V, Shimadzu, Japan). All of other detailed information about the HA sample can be found in previous studies (Yang et al., 2011).

### 2.2. Dissolution kinetics

For studying the dissolution kinetics of the three compounds,  $\text{CO}_2$  in Millipore water was removed by sparging with  $\text{N}_2$  for 24 h to minimize the influence of dissolved carbonate on the dissolution of these actinide borates. A background solution of 10 mM  $\text{NaNO}_3$  was made by directly dissolving the compound in the sparged water and pH value of the solution was adjusted to 7. Solutions of

20 mM bicarbonate and phosphate were prepared by dissolving a pre-determined amount of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{HPO}_4$  in the background solution. A solution of 20 mg C/L HA was made by diluting the stock solution of HA with the background solution of 10 mM  $\text{NaNO}_3$ . As there are large variations in the molecular weights of HA molecules, we cannot determine the exact molar concentration for HA (Yang et al., 2011). We used a natural environmentally-relevant concentration of 20 mg C/L for HA. All the solutions were readjusted to pH 7 with concentrated  $\text{HNO}_3$  or NaOH.

To analyze the kinetics for actinide borate dissolution, 5 mg of UBO or NaUBO or 2 mg of PuBO crystals were mixed with 20 mL of background, bicarbonate, phosphate, or HA solutions in headspace-free vials. The vials were tightly sealed to minimize the exchange between surrounding air and solutions. All the dissolution experiments were conducted at room temperature of  $23 \pm 2$  °C. According to the calculation for the equilibrium of  $\text{CO}_2$  between the atmosphere and the solution with pH 7, the possible exchange with surrounding air will result in no more than 0.016 mM bicarbonate in the solutions. The pH values of the solution samples with UBO/NaUBO were re-measured after the completion of dissolution experiments and no significant changes in pH values were detected, mainly due to the limited amount of dissolved crystals and the buffer capacity of the ligands we added.

For UBO and NaUBO, at different intervals up to 14 days, a small aliquot (0.5 mL) of the solution was sampled for aqueous U(VI) analysis. After 14 days of experiments, the residual crystals were harvested for further analysis. The harvested crystals were washed with Millipore water three times, and then rinsed with methanol three times. We were unable to collect enough crystals for characterization from the samples with bicarbonate.

For PuBO, at different intervals within eight days, 0.5 mL of solutions was sampled out for ICP-MS and UV-vis-NIR spectra analysis to demonstrate the concentration and speciation of Pu in the solutions. Upon completing the dissolution experiments, the residual PuBO particles were harvested and washed using the same method as for UBO and NaUBO before further analysis.

### 2.3. Aqueous phase analysis

For UBO and NaUBO, we used a PTI Quantamaster QM-4 spectrofluorometer for analyzing aqueous U(VI) concentration at different intervals (Gorby and Lovley, 1992; Sheng et al., 2011). A xenon flash lamp was used as an excitation source. The time-dependent intensity of phosphorescence emitted by U(VI) was recorded, with an excitation wavelength of 420 nm, emission wavelength of 515 nm and slit width of 17 nm. The detection limit was around 1 mg/L for U(VI).

Prior to analysis, the samples were centrifuged at 13,000 g for 3 min to remove possible suspending particles in solution samples. After that, 0.5 mL of sample was mixed with 0.25 mL of 12.1 M HCl and vortexed. Then the sample was diluted 200 times with Millipore water and 1 mL of the diluted solution was combined with 1.5 mL of Uraplex to strongly complex the uranyl ion and minimize other interferences. Thereafter, the samples were analyzed by the spectrofluorometer immediately. In order to analyze the species of aqueous U(VI), the solutions sampled after 14 days were further analyzed by Varian CARY 5000i scan UV-vis-NIR spectrophotometer. The absorption data were collected from 200 to 1400 nm.

For PuBO, a Thermo Finnigan high-resolution magnetic sector Element2 ICP-MS instrument was used to analyze the dissolved concentration of Pu at different intervals. TI was used as an internal standard. We conducted duplicate measurements for each sample and added a wash sample of 5%  $\text{HNO}_3$  per 12 samples. In order to further analyze the species of dissolved Pu(VI), liquid UV-vis-NIR spectra analysis was also applied for the solution samples, and the absorption spectra for Pu were collected from 400 to 1400 nm.

Download English Version:

<https://daneshyari.com/en/article/6436862>

Download Persian Version:

<https://daneshyari.com/article/6436862>

[Daneshyari.com](https://daneshyari.com)