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Aqueous Pu(IV) sorption on brucite

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Summary. The sorption behavior of aqueous Pu(IV) on brucite ($Mg(OH)_2$) in the presence and absence of citrate was investigated by a combination of wet chemical batch sorption experiments and X-ray photoelectron spectroscopy (XPS). Sorption occurs rapidly at near 100% levels from pH 8 to pH 13, and is not affected by the presence of citrate. XPS results indicate that Pu was incorporated in the subsurface in the cases studied.

Introduction

MgO, the currently used backfill/barrier material at the Waste Isolation Pilot Plant (WIPP) has the potential to retard actinide migration through sorption processes, but the effectiveness of MgO is not known. In an intrusion scenario, MgO is exposed to water, forming a variety of hydrated carbonate and/or hydroxide minerals, including brucite. This work investigates the effectiveness of brucite in reducing the solubility of actinides in the presence of waste-derived organic ligands. Citrate has been identified as one of the important water-soluble organic ligands in the WIPP waste inventory capable of increasing dissolved actinide concentrations [1] and it is a reasonable surrogate for other low molecular weight organic ligands. Pu is expected to be primarily tetravalent under the alkaline and reducing repository conditions, existing as the neutral hydroxide solution species ($Pu(OH)_4^0$) and perhaps in a polymeric Pu(IV) hydroxide colloid form [1]. In the experiments discussed, Pu was quickly sorbed on brucite, even in the presence of 10^{-3} M citrate. The nature of the absorbed Pu was investigated by XPS analysis of large, Pu-exposed brucite crystals. Angle resolved XPS and XPS sputter depth profiling indicated that Pu was incorporated in the bulk brucite to depths of at least 50 nm in one of the specimens.

Experimental

A Kratos XSAM800 X-ray photoelectron spectrometer system was used to collect the XPS data. High-resolution spectra were acquired at 20 eV pass energy using Mg K_α X-rays and an acceptance half-angle of 25°. No flood gun charge compensation was use in these measurements. Charge correction was performed by referencing the adventitious (hydrocarbon-like) carbon to 284.6 eV binding energy. Atomic concentration estimates were based on sensitivity factors appropriate for the instrumental conditions and analyzer design. The binding energy values [2–4] and sensitivity factor [3] used for the Pu 4*f* region were based on data derived from known Pu compounds, including PuO_2, $Pu(OH)_4$, and PuF_4.

Three different materials were used as substrates in this study: 1) colloidal brucite, 2) natural crystalline brucite and 3) hydroxylated MgO(100) single crystals. Colloidal brucite, obtained from National Magnesia Chemicals, had a mean particle diameter of 300 nm, as determined by dynamic light scattering, and a surface area of 25 m^2/g, as determined by N_2 gas adsorption. X-ray diffraction (XRD) indicated brucite as the bulk crystalline material, while X-ray photoelectron spectroscopy (XPS) results were consistent with a combination of brucite and periclase (MgO) at the near-surface, as compared to spectra obtained from standard materials.

Preparation of the MgO(100) single crystals for these studies simply involved exposure of the freshly cleaved surfaces to low-carbon deionized water in an Ar atmosphere for 24 hours. Samples prepared in this manner had brucite-like layers on their surfaces at least 35 Å thick, as determined by angle-resolved XPS.

The natural brucite crystals used in this work were cleaved in an Ar atmosphere from a rather large 2.5 cm × 0.5 cm translucent specimen that showed the expected trigonal tabular form with a slightly rounded hexagonal outline. The brucite structure is stacked sheets of octahedrons composed of Mg atoms bonded to six octahedrally coordinated hydroxide groups. Each hydroxide is bonded to three Mg atoms. The sheets are neutral and held together by weak bonds; this results in a soft, easily cleaved material.

Citric acid preparations were made using freshly prepared reagent-grade citric acid spiked with citric acid-1,5-^{14}C, obtained from Sigma. Stock solutions of 2 μCi/mL ^{14}C labeled citric acid in 1% ethanol were prepared from the original 50 μCi source using sterile glassware and pipette tips. This solution was stored at 4 °C in an autoclaved, brown glass vial. Working solutions of 4.4×10^4 dpm/mL ^{14}C citric acid were diluted from this stock and added to the freshly prepared unlabeled citric acid.

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Disproportionation, hydrolysis and colloid formation can make Pu(IV) solution chemistry quite complex. All four oxidation states can coexist in significant concentrations, depending on hydrogen ion concentration, Pu solution concentration, and complexation of the Pu ions. Pu oxidation state purity was evaluated by UV-Vis spectroscopy of a freshly prepared stock solution of 3×10^{-3} M Pu(IV) in 1 M $HClO_4$; no detectable Pu(III), Pu(V) or Pu(VI) was found. Pu working solutions of 5×10^{-5} M were prepared by dilution of the stock solution in 1 M $HClO_4$. Initial Pu(IV) concentration in the batch sorption experiments was 5×10^{-8} M, near the expected PuO_2 solubility limit for the existing solution conditions [1, 5]. The rates of both the disproportionation and the polymerization reactions are second order, dependent on Pu concentration [6]. The working solutions were stored at concentrations two orders of magnitude below the original measured stock solution, so loss of Pu(IV) though these mechanisms are probably not important. Reduction of Pu(IV) by alpha radiolysis may be significant, however. This process is estimated to result in a 1.4% loss per day [7] in the working solution. Oxidation state composition for the final working solutions used in the batch experiments is estimated at about 80% Pu(IV), and 20% Pu(III), based on this 1.4% alpha-induced reduction. In solutions with pH 3 or greater, such as those used for the batch experiments, Pu(III) is oxidized very rapidly by H_2O, producing Pu(IV) and ameliorating this loss.

Sorption experiments

General procedures

Batch sorption experiments were performed using sealable 30 mL polycarbonate Oak Ridge centrifuge tubes, each containing 30 g/L colloidal brucite and $NaClO_4$ at 0.1 M, which was used to provide constant ionic strength across the pH range of interest. Brucite mass concentrations were maintained at 30 g/L, resulting in a specific site concentration estimated at 3×10^{-3} M [8]. The pH of these solutions was monitored by calibrated Orion Ross combination electrodes and adjusted with small volumes of HCl or NaOH in order to span a pH range from 8–12, at increments of approximately 0.5 pH unit. After adding citric acid, Pu(IV) or a mixture of Pu(IV) and citric acid, the samples were raised to full volume (6 mL), set on a covered shaker table and allowed to come to equilibrium for an appropriate amount of time, based on results from simple kinetic experiments using the same solutions and solids. The tubes were sealed during equilibration to minimize exposure to atmospheric CO_2. After reaching equilibrium, the final pH of each tube was recorded, the solids were separated by centrifugation and the supernatants analyzed by liquid scintillation counting.

It was useful to compare the brucite sorption experiments to sorption and/or precipitation processes in the absence of brucite. Pu(IV) hydrolyzes readily above pH 1 and forms extended polynuclear hydroxo species at higher pH values. In the absence of solution carbonate species, the primary forms of Pu are probably the neutral $Pu(OH)_4$ and colloidal Pu(IV). Sorption to the container walls is expected to occur at about the same pH as the onset of hydrolysis. These experiments were carried out at much higher pH, between 8 and 13, so the blank experiments are a measure of Pu(IV) solubility under these conditions. After 54 hours equilibration, Pu concentrations decreased by about 40% in solutions with pH values between 8.5 and 9.5 and by 60%–70% in solutions with pH values between 9.5 and 11. Pu concentration losses observed above pH 11 in the same experiment were about 80%. In the presence of brucite, Pu concentrations decreased by 95% or more across the same pH range. Simple kinetic experiments performed at pH 10 showed the removal of over 95% of the soluble Pu in the first 2 min in the presence of brucite, while in the absence of brucite only 2% of the soluble Pu was removed during the same time period. Pu concentrations in the pH 10 blank (no brucite) tubes gradually decreased with time, as shown in Fig. 1, to about 60% of the original value after 54 hours.

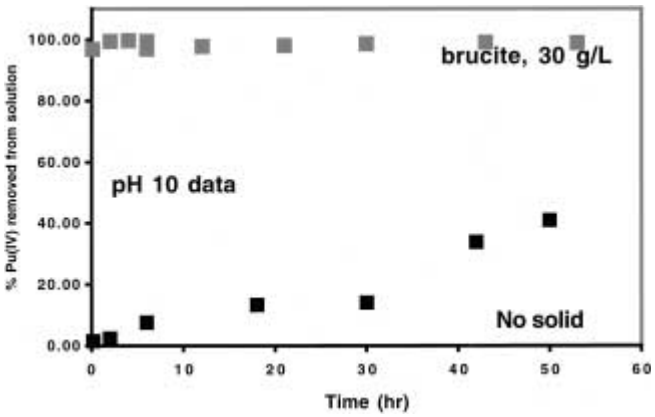

Fig. 1. Results of kinetic experiments performed at pH 10 showing the removal of over 95% of the soluble Pu in the first 2 min in the presence of brucite, while in the absence of brucite only 2% of the soluble Pu was removed during the same time period. Pu concentrations in the pH 10 blank (no brucite) tubes gradually decreased with time, to about 60% of the original value after 54 hours.

Results and discussion

Citrate on brucite

Fractional citrate sorption as a function of pH is shown in Fig. 2a. The sorption is fairly constant at about 90% above pH 10, but drops off to about 60% at lower pH values. This trend manifested itself in three other sets of data taken under the same conditions. The shape of this curve is atypical of anion sorption to metal oxide surfaces. The behavior exhibited is likely the consequence of brucite dissolution as the system approaches circumneutral pH values.

Pu(IV) on brucite

Pu(IV) sorption was essentially complete across the entire pH range measured, as illustrated in Fig. 2b, and independent of the Pu/brucite ratio or ionic strength. Mass balances for Pu were performed on solutions from selected tubes by dissolving the solids and leaching the walls with acid. In all cases, greater than 99% of the Pu was found with the brucite. The identity of Pu species associated with the brucite is unknown. At an initial concentration of 5×10^{-8} M, we are below the range where optical absorbance methods can easily be used. As mentioned previously, Pu can exist in a variety

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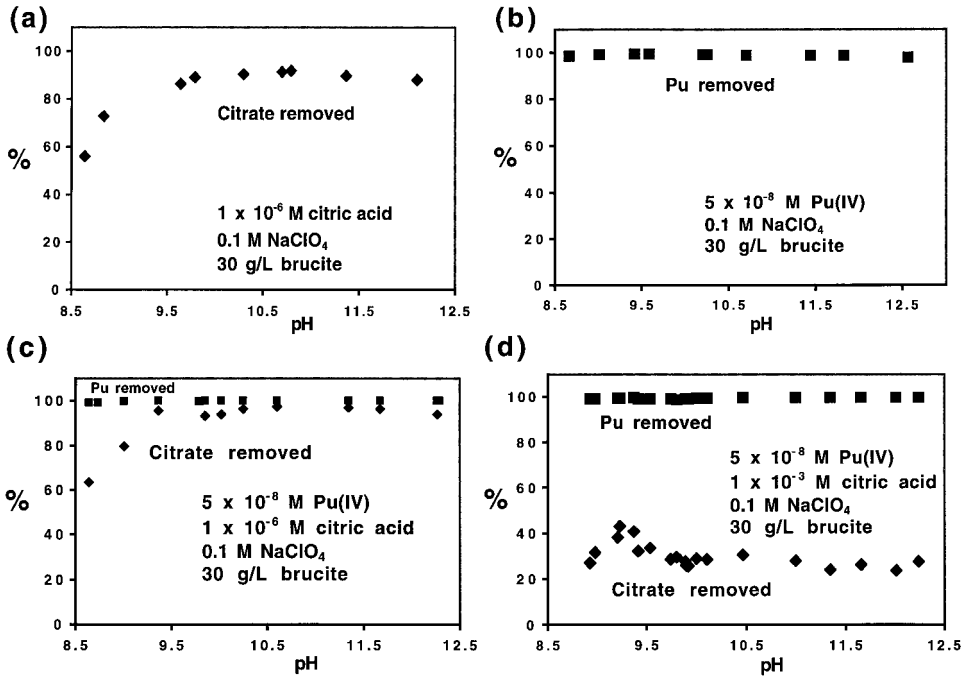

Fig. 2. Fractional sorption of citrate and/or Pu(IV) on brucite as a function of pH. Brucite loading and solution composition were all 30 g/L and 0.1 M $NaClO_4$, respectively. (**a**) 10^{-6} M citrate on brucite. Sorption decreases as the solid brucite begins to dissolve. (**b**) 5×10^{-8} M Pu(IV) sorption on brucite. Note the near complete removal of Pu from solution across the entire pH range. (**c**) 5×10^{-8} M Pu(IV) sorption on brucite in the presence of 10^{-6} citrate. Citrate has no apparent effect on Pu sorption. (**d**) Pu(IV) (5×10^{-8} M) sorption on brucite in the presence of 10^{-3} citrate. Citrate levels were near the calculated site density of the brucite solid, resulting in decreased fractional sorption.

of forms and oxidation states. Under these alkaline conditions and in the absence of solution carbonate species, the primary forms of Pu are probably the neutral $Pu(OH)_4$ and colloidal Pu(IV). The polymerization reaction is expected to be more important than the disproportionation reactions, but both of these processes take time and are second-order, dependent on concentration, so polymerization is less probable. When brucite is available, Pu concentrations decrease dramatically. Possibilities include sorption of individual Pu ions, polymerization (colloid formation) before sorption or polymerization/precipitation after sorption. Recrystallization of the dynamic brucite surface may also result in the incorporation of Pu, whatever its form, as part of the brucite solid.

Pu(IV) and citrate on brucite

The formation of strong metal-ion/ligand complexes has long been known to affect metal-ion sorption to particle surfaces. The log stability constant ($\beta_2 = [PuCit_2]/[Pu][Cit]^2$) for Pu(IV)/citrate complexes in 0.5 M $NaClO_4$ is about 30.1 [9]. Pu(IV)/citrate complexation is well known [7], and some recent work [10] suggests that citrate forms complexes with Pu(IV) colloids. Pu(IV)-citrate complexation is generally less effective above pH 8, however, and, as shown below, did not play an important role under the alkaline conditions of these experiments.

Figs. 2c and 2d present the results of experiments in which Pu and citrate are co-solutes. A comparison of Figs. 2c and 2d shows that Pu sorption by brucite is unaffected by the Pu/citrate ratio even at citrate concentrations approaching the estimated available brucite site concentration at 30 g/L (approximately 10^{-3} M). Additional experiments demonstrated that the results shown in Figs. 2c and 2d do not depend on the order of component addition.

Spectroscopic investigations

Sample preparation for these experiments deviated from the conditions used in the batch experiments in several respects. Higher citrate and/or Pu solution concentrations were needed to assure detection by XPS. In order to get reliable information about the chemistry of surface species, concentrations of the elements of interest at or near the surface must be at least 0.1 atomic %; thus, acidic solutions were used to maintain these higher Pu concentrations. There are strong correlations, however, between the spectroscopic sample conditions and the conditions that existed in the low pH (8–9) region of the batch experiments. In the batch experiments, a small amount of Pu(IV) in acid was quickly injected and mixed with the alkaline, brucite-containing solutions in the centrifuge tubes. The local environment near the surfaces of the brucite crystals (whether they are in bulk or colloidal form) will be alkaline, probably near pH 10. Pu ions exposed to this elevated pH will tend to hydrolyze immediately and then sorb on the brucite surface. The polymerization reaction for Pu at 10^{-8} M is slow, so colloid formation under these conditions is negligible. Solutions containing Pu(IV) and crystalline brucite or hydroxylated MgO crystals for the spectroscopic studies started at low pH, but became more alkaline over the course of exposure, finally reaching measured pH values between 8 and 9. As in the batch experiments, Pu ions were presumed to have been exposed to a highly alkaline micro-environment near the surfaces of the crystals. Furthermore, the crystals are well-

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rinsed with Mg-saturated solutions (pH 10.2) when removed from the Pu solutions. This process is required to wash away electrolyte (acid) deposits which would interfere with the XPS analysis. Weakly-bound Pu is also removed leaving only the relevant inner sphere adsorbed Pu complexes or Pu that was incorporated into the crystal.

Citrate on brucite

A freshly-cleaved brucite crystal was exposed to solutions of 0.1 M citric acid then rinsed with a Mg(II)-saturated solution. XPS data collected from the C 1*s* region showed an additional peak, when compared to unexposed crystals, at about 288.4 eV after this treatment, indicating the presence of carboxyl groups on the surface. Citrate most likely binds to the surface by its extreme carboxylate groups [11], but binding can occur with any or all of its functional groups. The presence of these carboxyl groups on the surface is a strong indication that citrate sorption has occurred. The nature of the brucite/citrate bonding is still under investigation.

Pu(IV) on (and in) brucite

Freshly-cleaved brucite and hydroxylated MgO crystals were immersed in solutions of 10^{-5} M ^{239}Pu(IV) in 0.1 M $HClO_4$. After 5 hours, the crystals were removed from the solutions (now ranging in pH from 8.1–9.1) and rinsed with Mg(II)-saturated water to remove the weakly-bound species. After drying in air, alpha activity was monitored by a probe that was set a fixed distance above the samples. These simple surveys showed alpha activity ranging from a few hundred to a few thousand counts per minute, yielding rough measures of Pu sorption levels. The range for 5 MeV alpha particles in brucite is about 5×10^4 nm, according to TRIM simulations [12], so alpha surveys can detect Pu below the surface at significant depths. XPS, on the other hand, is sensitive only to the outermost atomic layers. For these investigations, the analysis depth was about 4 nm.

XPS results

Information about the chemical state of Pu in the outermost layers of one of the brucite crystals was obtained by analysis of the Pu 4*f* core level. Fig. 3 shows spectra from several different photoemission angles from the brucite surface. The spin-orbit splitting of the 4*f* level is apparent in the 5/2 and 7/2 peaks seen at about 439 and 426 eV, respectively. Pu(IV) is the dominant oxidation state, as evidenced by the distinctive satellites seen about 7 eV above the main two peaks, with a chemical shift between that expected for Pu hydroxide and Pu dioxide.

Pu surface concentrations, measured by XPS (which has a much shallower analysis depth than the alpha measurements by a factor of 10^4), were estimated at less than 1 atomic %. These results sharply contrast with measurements made on oxidized silicon that had been exposed to the same Pu(IV) solution and showed nearly the same alpha activity after exposure as the brucite. Photoemission intensity for the Pu 4*f* lines from the SiO_2 surface were an order of magnitude higher than those from brucite, yielding concentration estimates of 5 atomic % on the surface. These results suggest that Pu was incorporated in the brucite subsurface, with most of the Pu being deeper than the analysis depth of XPS, but still detectable in the alpha emission.

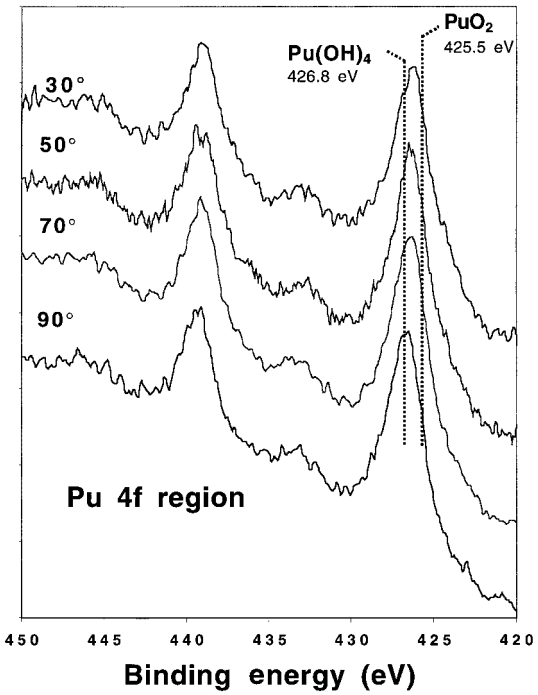

Fig. 3. XPS spectra of the Pu 4*f* core levels obtained from the surface of natural crystalline brucite at photoelectron take off angles of 30°, 50°, 70°, and 90° relative to the surface plane. This sample was exposed to 10^{-5} M Pu(IV) for 5 hours. The vertical lines indicate binding energy values where the $4f_{7/2}$ peaks are expected for PuO_2 and $Pu(OH)_4$. Surface and near-surface Pu is primarily tetravalent, with a chemical state between the dioxide and hydroxide.

Angle resolved photoemission measurements also supported the concept of Pu subsurface incorporation. XPS showed that Pu was distributed throughout the analysis depth of about 40 Å, and was only slightly more concentrated in the outermost layers. The analysis depth was varied from about 20 Å to about 40 Å as the photoelectron take-off angle was adjusted from 30° to 90° in 20° increments. Pu/Mg atomic ratio estimates, derived from peak areas for the Pu $4f_{7/2}$ and Mg 2*p* regions, ranged from 0.03 for the 30° take-off angle to 0.02 for the 90° angle. As the effective analysis depth becomes shallower at 30°, Pu shifts slightly from the more ionic hydroxide-like form towards a more covalent dioxide-like state.

Angle resolved XPS of the hydroxylated MgO(100) crystal exposed to Pu(IV) under the same conditions showed no Pu concentration gradient with respect to Mg. XPS estimates of Pu concentrations were less than 1 atomic %, although alpha counts were again high, indicating that Pu was incorporated in the bulk. Binding energies and satellite intensities for the Pu 4*f* lines were consistent with Pu(IV), with a chemical state between the dioxide and hydroxide.

XPS sputter depth profiling was performed on a brucite crystal that had been exposed to 10^{-5} M Pu(IV) for 7 hours. Depth profiling was accomplished by alternatively sputtering the surface with 5 kV Ar ions and collecting data over the Pu 4*f*, O 1*s*, Mg 2*p*, and C 1*s* regions. Sputter

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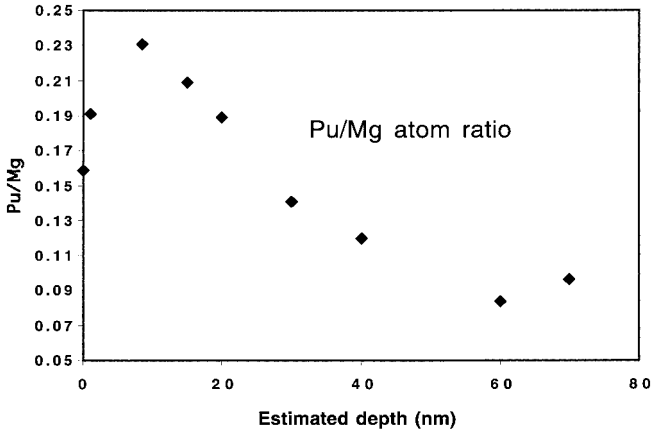

Fig. 4. XPS sputter-etch depth profile obtained from the surface of a brucite crystal that had been exposed to 10^{-5} M Pu(IV) for 7 hours, rinsed with Mg(II)-saturated water and dried under Ar. Pu has become incorporated in the brucite crystal to significant depths with a maximum concentration appearing about 10 nm below the surface.

rate estimates were based on comparisons with etch rates on Ta_2O_5 films of known thickness under the same conditions. The results of the profile, shown in Fig. 4, show that Pu was detected below the original surface at depths 50–70 nanometers. Pu concentrations reach a maximum of about 7 atomic % just below the original surface. The process of washing the crystals with Mg(II)-saturated DI water after the exposure may have the effect of slightly replenishing the Mg-depleted surface layers thus depleting the Pu concentrations in the outermost region.

Conclusion

These experiments have shown that Pu(IV) is sorbed rapidly and completely by brucite from pH 8.5 to pH 12.5. Additionally, sorption of Pu(IV) by brucite in this pH range is unaffected by the presence of citrate. XPS analyses of the single crystal brucite and hydroxylated MgO exposed to Pu-containing solutions indicate that the solid sorbs the Pu in a (IV) oxidation state. It was also shown that the Pu was incorporated into the crystal subsurface at a substantial concentration to a depth of at least 50 nm. The specific mechanism and chemistries of this incorporation are not yet understood. Brucite (or hydroxylated MgO) has the potential to be an effective retardant at TRU waste repositories.

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References

1. *Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant, Appendix SOTERM* (1996). US-DOE Carlsbad Area Office 1996–2184.
2. Cox, L. E., Farr, J. D.: $4f$ Binding-Energy Shifts of the Light-Actinide Dioxides and Tetrafluorides. Phys. Rev. B **39**, 11142 (1989).
3. Farr, J. D., Cox, L. E.: Core-Level Binding-Energy Shifts of the Light Actinide Tetrafluorides and Dioxides. Los Alamos National Laboratory Report LA-11677-MS (1989).
4. Farr, J. D., Schulze, R. K., Neu, M. P.: Unpublished data.
5. Nitsche, H., Roberts, K., Xi, R., Prussin, T., Becraft, K., Al Mahamid, I., Silber, H. B., Carpenter, S. A., Gatti, R. C.: Long Term Plutonium Solubility and Speciation Studies in a Synthetic Brine. Radiochim. Acta **66**/**67**, 3 (1994).
6. Newton, T. W., Rundberg, V. L.: *Disproportionation and Polymerization of Plutonium(IV) in Dilute Aqueous Solutions*, Mater. Res. Soc. Symp. Proc., Vol. 26, Published by Elsevier Science Publishing Co., Inc. (1984)
7. Cleveland, J. M. [1980]: Solution Chemistry of Plutonium. *Plutonium Handbook* (Wick, O. J., ed.).
8. Davis, J. A., Kent, D. B.: Surface Complexation Modeling in Aqueous Geochemistry. In: *Reviews in Mineralogy* (Hochella, M. F., White, A. F., eds.). Mineralogist Society of America, Washington, D. C., 1990, pp. 177–260.
9. Martell, A. E., Smith, R. M.: *Critical Stability Constants, Vol. 3: Other Organic Ligands*. Plenum Press 1977, 1989.
10. Neu, M. P., Schulze, R. K., Conradson, S., Farr, J. D., Haire, R. G.: Polymeric Pu(IV) hydroxide: Formation, Prevalence, and Structural and Physical Characteristics. Presented at Pu Futures, sponsored by LANL in Santa Fe, NM (1997).
11. Cornell, R. M., Schindler P. W.: *Infrared Study of the Adsorption of Hydrocarboxylic acids on Alpha-* FeOOH *and Amorphous* Fe(III)*hydroxide.* Colloid. Polym. Sci. **258**, 1171 (1980).
12. Ziegler, J. F., Biersack, J. P.: *The Stopping and Range of Ions in Solids (TRIM).* Pergamon Press, New York, 1985.

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