Reduction of Actinide(VI) Species in the Waste Isolation Pilot Plant (WIPP)

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Introduction

Experiments were performed at Argonne National Laboratory to establish the empirical solubility and redox stability of U(VI), Np(VI), and Pu(VI) in sodium-chloride-magnesium brine.[1,2] Steady-state actinide concentrations that were defined by the precipitation of amorphous phases were often observed. Synchrotron-based methods, namely, x-ray absorption near-edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS), were used to identify the predominant oxidation states over time in these complex "real-system" samples and, when possible, establish the identity of the phase.

The oxidation state of the actinide phases formed was a key parameter for the performance assessment that was used to license the Waste Isolation Pilot Plant (WIPP) as a repository for transuranic nuclear waste. Models developed by the WIPP were oxidation-state specific and relied on the predicted distribution of oxidation states in the subsurface to establish the source term concentration and, therefore, predict the rate of actinide release. In this context, the XANES spectra provided valuable confirmation that reduction, hence, immobilization was likely under the conditions prevalent in the WIPP.

Methods and Materials

Actinide(VI) aqueous species were prepared and added to WIPP brine in a nitrogen glovebox to minimize oxygen in the system. Experiments were performed in the dark, with ~ 1 atm. hydrogen overpressure, in low and high magnesium brines, at pH 5 to 10, in the absence/presence of carbonate, and for up to 18 months. Initial actinide concentrations were 0.1 mM. The total actinide concentration was monitored using inductively coupled plasma-mass spectrometry, and alpha scintillation counting methods. The oxidation state present was monitored by absorption spectrometry on a CARY5 spectrometer.

At the end of the experiment, the precipitates, if present, were collected by centrifugation. They were then triply encapsulated in a polystyrene matrix and transported to the Advanced Photon Source (APS) for analysis. XANES/EXAFS analyses were performed on the MR-CAT undulator beamline at the APS.

Results

The various actinide(VI) species did not exhibit the same redox stability under the conditions of our WIPP experiments. In many cases, precipitate formation led to lower steady state concentrations of the actinide in solution. Analyses of the amorphous precipitates by XANES were used to establish the predominant oxidation state. This information was needed to distinguish between reduction, sorption, and precipitation as the key mechanism controlling aqueous actinide concentrations.

Uranium(VI) was stable as an aqueous species at pH 5 and 7 but precipitated at pH 8 and 10. The XANES analyses of the precipitates recovered are shown in Fig. 1. There is a good match between the XANES spectrum of the precipitates collected and the U(VI) oxy-hydroxide precipitate used as a standard. This result indicated that the steady-state concentrations for uranium(VI) were being determined by the solubility of the U(VI) phase rather than reduction.

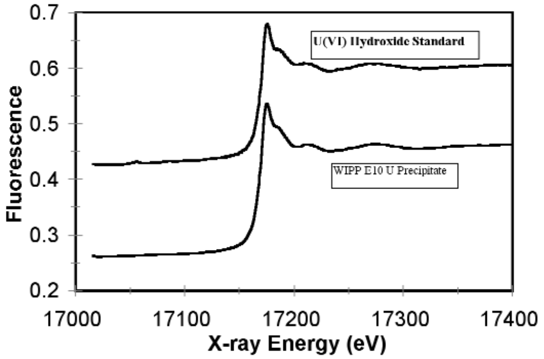

FIG. 1. Comparison of the XANES spectrum of U(VI) hydroxide precipitate standard and the unknown precipitate from a long-term WIPP experiment at pH 10 in ERDA-6 brine.

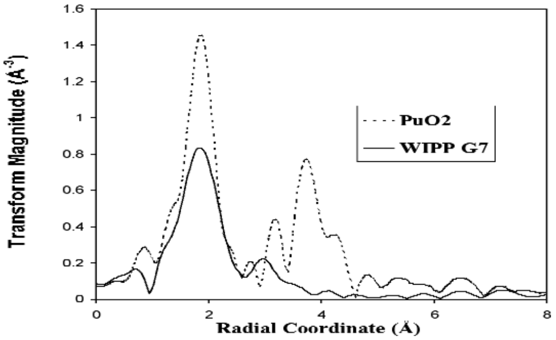

FIG. 2. Radial distribution (EXAFS) of plutonium precipitates collected from the pH 7 WIPP experiments containing iron and plutonium(IV) oxide. The XANES of the WIPP precipitates (not shown) correlated with the Pu(IV) oxidation state edge and indicate that reduction leading to precipitation occurred.

Neptunium(VI) was not stable under any of the experimental conditions examined. Reduction to Np(V) in solution led to the formation of amorphous precipitates at high pH. The XANES analysis of the various phases collected indicated that Np(V) was the predominant phase. This finding confirmed partial reduction leading to lower solubility.

Plutonium(VI), when no reducing agent was present, was stable under all conditions investigated in WIPP brine—so no precipitation was noted. Iron coupons were added to these solutions to establish the effect of the iron containers present in the WIPP on the oxidation state distribution. This addition led to an almost four orders of magnitude decrease in the plutonium concentrations and precipitation of plutonium phases. The XANES analysis of the plutonium precipitate and the plutonium sorbed onto the iron surface indicated that the Pu(VI) had been reduced to Pu(IV). Figure 2 shows the EXAFS analysis, in radial space, of the precipitate obtained at pH 7 compared to that of the plutonium(IV) oxide standard. Although there was a good match in Pu-O bond lengths, the pH 7 WIPP sample had much greater disorder, confirming the amorphous nature of the precipitate. The XANES edge analysis confirmed that the oxidation state of the amorphous precipitate was Pu(IV).

Discussion

The XANES spectra were used to identify the primary oxidation state in WIPP amorphous solids that were otherwise difficult to establish. These data show that the higher oxidation states of Np, Pu, and U can predominate, and it is their solubility that defines the source term concentrations in WIPP brine. There is good agreement between the steady-state concentrations we measured and the calculated solubility for a given oxidation state. For plutonium(VI), the presence of iron was an effective reducing agent leading to the formation of Pu(IV) and much lower solubility. Our concentration data also showed good agreement with solubility predictions made by the WIPP model for Pu(IV) phases.

Acknowledgments

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References

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