Reduction of plutonium(VI) in brine under subsurface conditions

By D. T. Reed[1,*], J. F. Lucchini[1], S. B. Aase[2] and A. J. Kropf[2]

[1] Earth and Environmental Sciences Division, Los Alamos National Laboratory, Carlsbad NM 88220, USA
[2] Chemical Technology Division, Argonne National Laboratory, Argonne IL 60439, USA

Summary. The redox stability of PuO_2^{2+} was investigated in brine under subsurface conditions. In simulated brines, when no reducing agent was present, 0.1 mM concentrations of plutonium(VI) were stable as regards to reduction for over two years, which was the duration of the experiments performed. In these systems, the plutonyl existed as a carbonate or hydroxy-chloride species. The introduction of reducing agents (*e.g.* steel coupons, and aqueous Fe^{2+}) typically present in a subsurface repository, however, led to the destabilization of the plutonium(VI) complexes and the subsequent reduction to Pu(IV) under most conditions investigated. X-ray Absorption Near-Edge Spectroscopy (XANES) confirmed that the final oxidation state in these systems was Pu(IV). This reduction lowered the overall steady state concentration of plutonium in the brine by 3–4 orders of magnitude. These results show the importance of considering repository constituents in evaluating subsurface actinide solubility/mobility and provide further evidence of the effectiveness of reduced iron species in the reduction and immobilization of higher-valent plutonium species.

1. Introduction

The fate and transport of multivalent actinides such as plutonium, which can exist in the +3, +4, +5 and +6 oxidation state under subsurface conditions, is largely defined by the redox conditions present in the subsurface. The most important subsurface processes that define the redox environment are geochemical-host rock interactions [1–5], reactions with organics, humics, and fulvics [6, 7], and direct and indirect effects of biological processes [8, 9]. Under reducing conditions, plutonium is expected to be reduced to predominantly Pu(III) and Pu(IV) species that are sparingly soluble under most subsurface conditions.

Although the predominance of reduced species under most anoxic subsurface conditions is both expected and predicted, the mechanisms by which this reduction occurs and, in the longer-term sustained, are not fully understood. In particular, the role of reduced metals such as iron and manganese, which are often identified as the likely reducing agents of other metals in the subsurface, is not well understood under basic conditions. The Waste Isolation Pilot

Plant (WIPP) repository has attributed the predominance of reduced multivalent actinides (primarily in the +3 and +4 oxidation state) in their performance assessment [10, 11] to the co-existence of high amounts of iron in transuranic (TRU) waste. Zero valent iron has also received attention as a subsurface barrier material for multivalent metals [12, 13]. The ability and extent that Pu(VI) is reduced to Pu(IV) by iron has also been questioned [14]. It is a key goal of the research reported herein to determine the role of iron in establishing the predominant plutonium species under subsurface conditions.

Herein, we report the results of two studies that were done in sequence to investigate the fate of plutonyl (PuO_2^{2+}) in brine. Initially, over a two year timeframe, the redox stability of PuO_2^{2+} was determined as a function of pH and brine composition. Subsequently, repository components (*e.g.*, iron and MgO) were added to these equilibrated systems to establish their effect on the oxidation state distribution and effective solubility. These investigations complement and extend past studies [6, 15–17] to establish the oxidation state distribution of plutonium in brine.

2. Experimental methods

The experiments performed in the two sequential studies, along with some experimental conditions, are listed in Table 1. Plutonium-239 (> 99% purity by activity and mass) was used in all of the experiments. Plutonium was oxidized to PuO_2^{2+} by fuming in perchloric acid to near-dryness and dissolved in 0.1 M HCl. G-Seep and ERDA-6 simulated brine (see Table 2) were made using high purity reagent grade Aldrich Chemicals compounds. Iron, when added, was in two forms: steel coupon (ASTM A366 lot J) typical of the material used for containers in the WIPP, and Aldrich reagent grade iron (II) chloride. High purity reagent grade MgO was used for the MgO experiments.

The experimental approach in the first set of experiments was to add a Pu(VI) spike to brine as a function of pH, brine composition, and presence/absence of carbonate (see Table 1) and monitor the oxidation state and total concentration as a function of time to establish its redox stability. In experiments with no added carbonate, the PuO_2^{2+} acid stock solution was added to 3 mL of the brine of interest to check for precipitation. An additional 7 mL of the brine was then

---

*Author for correspondence (E-mail: dreed@lanl.gov).

Table 1. Experimental Matrix to Determine the Stability of Pu(VI) in Brine[a].

Pu(VI) Stability experiments		Pu(VI) Interaction studies	
Experiment Designation	Description[b]	Experiment Designation	Description
PU-G5	10^{-4} M Pu(VI) in G-Seep brine at pC_{H^+} 5	G5-B G5-FE G5-FE2	PU-G5 Blank PU-G5 with low carbon steel coupon PU-G5 with added Fe^{2+}
PU-G7 and PU-G7-NC	10^{-4} M Pu(VI) in G-Seep brine at pC_{H^+} 7	G7-B G7-FE G7-FE2	PU-G7 Blank PU-G7 with low carbon steel coupon PU-G7 with added Fe^{2+}
PU-E8	10^{-4} M Pu(VI) in ERDA-6 brine at pC_{H^+} 8 and 10^{-3} M Carbonate	E8-B E8-FE E8-FE2 E8-MGO	PU-E8 Blank PU-E8 with low carbon steel coupon PU-E8 with added Fe^{2+} PU-E8 with added MgO powder
PU-E10	10^{-4} M Pu(VI) in ERDA-6 brine at pC_{H^+} 10 and 10^{-3} M Carbonate	E10-B E10-FE E10-FE2 E10-MGO	PU-E10 Blank PU-E10 with low carbon steel coupon PU-E10 with added Fe^{2+} PU-E10 with added MgO powder
PU-E10-NC	10^{-4} M Pu(VI) in ERDA-6 brine at pC_{H^+} 10 with no added Carbonate	E10NC-B E10NC-FE E10NC-FE2	PU-E10-NC Blank PU-E10-NC with low carbon steel coupon PU-E10-NC with added Fe^{2+}

a: All experiments were performed at $30 \pm 2\,°C$, with Pu-239, in a once-through nitrogen glovebox;
b: pC_{H^+}, is the measured pH corrected for ionic strength effects; $pC_{H^+} = pH_{measured} + 0.9$.

Table 2. Nominal Composition of the Simulated WIPP Brines.

Element, Species, or Property	ERDA-6[a] M		G-Seep[b] M	
	Actual	10% Diluted	Actual	10% Diluted
Cl^-	4.64	4.18	5.07	4.56
SO_4^{2-}	0.167	0.150	0.297	0.267
B	0.063	0.057	0.14	0.13
CO_3^{2-}/ HCO_3^-	0.016	0.014	0	0
Br^-	0.011	0.010	0.017	0.015
Na^+	4.85	4.37	4.18	3.76
K^+	0.097	0.087	0.338	0.304
Mg^{2+}	0.019	0.017	0.612	0.551
Ca^{2+}	0.012	0.011	0.0077	0.0069

a: This is a Castile synthetic brine. Initial pC_{H^+} will be 8 and 10;
b: This is a Salado synthetic brine. Initial pC_{H^+} will be 5 and 7.

added (total of 10 mL), transferred to the nitrogen glovebox, and bubbled with high-purity nitrogen to remove air. For experiments that contained carbonate, the PuO_2^{2+} was first diluted into 3 mL of a high carbonate solution to form a carbonate complex and then combined with 7 mL of the brine of interest. This was checked for precipitation, transferred to the nitrogen glovebox and bubbled with nitrogen to remove air.

The stability experiments were performed in 1.0 Liter polypropylene bottles that had been inserted in 1.8 Liter Hastelloy Parr vessels that were located in a temperature-controlled $(25 \pm 0.5\,°C)$ once-through nitrogen glovebox plumbed for gas and liquid sampling. Significant care was given to remove traces of oxygen and carbon dioxide from these vessels prior to the addition of brine. This was done by a sequential pump down and re-equilibration with high-purity nitrogen gas over a period of over two months. Approximately 750 mL of each brine was bubbled with

nitrogen in the glovebox and added through a Teflon tube into the various vessels. These brines were pumped down to remove any remaining gas by sequential vacuum expansion and re-equilibrated with high purity nitrogen. The 10 mL of de-aerated plutonium stock solutions were added through the same Teflon tube. After the plutonium was added, the solution was de-gassed by sequential vacuum expansion, and a 950 ± 50 torr hydrogen atmosphere was added. The gas phase was monitored throughout the experiment by periodic sampling and analysis by gas chromatography (Varian model 3300 and 3400 configured with a thermocouple detector). Although trace levels of nitrogen and carbon dioxide (when present in solution) were detected in the hydrogen gas samples, no oxygen was detected. Periodically, ~ 5 mL of solution was removed from the vessel using a Teflon tube connected to a de-aerated syringe. This sample was partitioned to measure pH using a Ross combination electrode; measure dissolved carbonate (acidification followed by carbon dioxide analysis); measure plutonium concentration as a function of filtration (unfiltered, 0.2 μm and 20 nm Millipore centrifuge filters) and a Packard 2π alpha scintillation counter which was supported by ICP-MS analysis; and plutonium oxidation state, using a gas-tight cuvette to prevent re-exposure to oxygen, with a CARY 5 UV-Vis-NIR spectrometer.

After two years of equilibration under anoxic conditions, we conducted a series of plutonium interaction studies with components that typically coexist with TRU waste to evaluate their effect on the observed stability of the Pu(VI) oxidation state (see Table 1 for the experimental matrix). These experiments were conducted by transferring ~ 20 mL of solution from the 2-year equilibration studies into a 30 mL polypropylene bottle that had been pre-equilibrated with brine and placed in a nitrogen glovebox to remove air. All of this was done in a nitrogen glovebox to maintain anoxic conditions throughout. The effects of the following three

constituents were investigated: 1) zero-valent iron in A366 steel, 2) Fe^{2+} suspensions, and 3) high purity MgO. In these experiments a small aliquot of the solution was periodically removed and sequentially filtered through 20 nm filters under anoxic conditions. The same procedures were used for solution analysis as in the first set of experiments.

3. Results and discussion

3.1 Stability of Pu(VI) in the absence of reducing agents

The results of the Pu(VI) stability experiments are summarized in Table 3. The concentration of plutonium as a function of time is shown in Fig. 1 in G-Seep and ERDA-6 brine. The concentration of plutonium, as a PuO_2^{2+} species, in both G-Seep and ERDA-6 brine was predominantly stable over the two-year duration of the experiments. The plutonium concentration in these experiments was below saturation and steady-state concentration limits were not established.

The aqueous speciation of plutonium in the brine experiments varied as a function of pC_{H^+} and carbonate concentration. At pC_{H^+} 8 and 10, in the presence of carbonate (experiments Pu-E10 and Pu-E8), the absorption spectra are essentially identical and correspond to a Pu(VI) carbonate species. At pC_{H^+} 10, in the absence of carbonate (experiment Pu-E10-NC), a Pu(VI) hydroxy-chloride complex was observed. There is no spectroscopic evidence for the reduction of Pu(VI) for all three ERDA-6 brine experiments under the conditions investigated.

A hydroxy-chloride Pu(VI) complex is present in the replicate experiments (Pu-G7 and Pu-G7-NC) in G-Seep brine at pC_{H^+} 7. A small decrease in total plutonium concentration was evident at long times. There was also spectral evidence for the formation of Pu(V), presumably due to autoradiolysis effects, in solution. The formation of Pu(V)
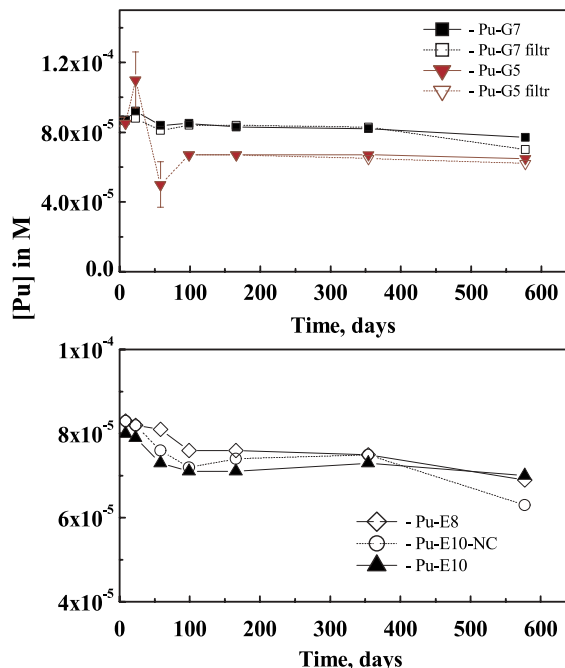

Fig. 1. Top: Concentration of plutonium as a function of time in G-Seep brine (experiments Pu-G5, Pu-G7 and Pu-G7-NC). Significant differences in concentration due to filtration were noted in the experiments at long times but were not present in the initial concentration data. Bottom: Concentration of plutonium as a function of time in ERDA-6 Brine (experiments, Pu-E10, Pu-E8 and Pu-E10-NC). No significant differences in concentration were noted between the unfiltered, $0.2\,\mu$ filtered and 20 nm filtered solutions.

may account for the small decrease in total concentration since this would lead to the formation of some Pu(IV) precipitates as a consequence of dis-proportionation reactions. At pC_{H^+} 5 (experiment Pu-G5), total concentrations decreased by $\sim 25\%$. The speciation, based on the absorption spectra is similar to that observed at pC_{H^+} 7 except that

Table 3. Summary of Results from the Pu(VI) Equilibration Studies in Brine.

Experiment designation and description	$pC_{H^+}^a$ (± 0.1)	$[CO_3^{2-}]^b$ and $[HCO_3^-]$	Initial $[Pu]^c$ in M + 5%	Final [Pu] in M as a function of filtration – uncertainty is $\pm 5\%^c$			Spectroscopy and predominant oxidation state in solution
				Unfiltered	0.2 µm	20 nm	
PU-G5 G-Seep brine at pC_{H^+} 5	5.2	$< 1 \times 10^{-6}$ M	8.7×10^{-5}	6.7×10^{-5}	6.7×10^{-5}	6.7×10^{-5}	Pu(VI) hydroxy-chloride species with some Pu(V) (estimated to be $\sim 20\%$)
PU-G7 and PU-G7-NC G-Seep brine at pC_{H^+} 7	7.1	$< 1 \times 10^{-6}$ M	8.7×10^{-5}	8.3×10^{-5}	8.4×10^{-5}	8.3×10^{-5}	Pu(VI) hydroxy-chloride species with some Pu(V) (estimated to be $\sim 10\%$)
PU-E8 ERDA-6 brine at pC_{H^+} 8 and 10^{-3} M Carbonate	8.1	0.0073 M	8.3×10^{-5}	7.6×10^{-5}	7.6×10^{-5}	7.6×10^{-5}	Pu(VI) carbonate complex with no evidence of Pu(IV/V)
PU-E10 ERDA-6 brine at pC_{H^+} 10 and 10^{-3} M Carbonate	10.1	0.0021 M	7.9×10^{-5}	7.0×10^{-5}	7.1×10^{-5}	7.3×10^{-5}	Pu(VI) carbonate complex with no evidence of Pu(IV/V)
PU-E10-NC ERDA-6 brine at pC_{H^+} 10 without added carbonate	10.1	$< 1 \times 10^{-6}$ M	8.3×10^{-5}	7.4×10^{-5}	7.4×10^{-5}	7.6×10^{-5}	Pu(VI) hydroxy-chloride species with no evidence of Pu(IV/V)

a: pC_{H^+} measured throughout the experiments was within 0.1 pC_{H^+} of the initial pC_{H^+} (pH measurements corrected for ionic strength);
b: The limit of detection for the carbonate acidification method was 1×10^{-6} M;
c: These data are based on liquid scintillation counting data.

a lower concentration of Pu(V) is present suggesting that Pu(IV) may be forming more rapidly.

The long-term stability, or perhaps more accurately meta-stability, of Pu(VI) in WIPP brine is consistent with results reported previously in slightly different brines [15]. The plutonium predominantly existed in solution as spectroscopically recognizable hydroxy-chloro or carbonato species that were filterable to 20 nm. This is not surprising given the strong tendency of Pu(VI) to undergo hydrolysis and form carbonate complexes in the pH range investigated.

We do not believe radiolysis played the key role in the observed stability of Pu(VI) in our systems. Since we started the experiment with ∼ 100% Pu(VI), if anything, radiolysis was the predominant pathway for the reduction of Pu(VI) that was noted in the lower pH experiments with no carbonate present. Oxidation state distribution in irradiated systems is determined by the sum of the effects of transient reducing/oxidizing species and the effects of molecular products accumulated over time (*e.g.*, oxy-chlorides in NaCl brines). Since we started with only Pu(VI), it is not unreasonable to expect some steady state concentration of Pu(V) due to the effects of the strongly reducing transients generated radiolytically. This is also consistent with our observation that this effect was much less at higher pH where the Pu(VI) is more strongly complexed and lower reactivity with the radiolytic transients is expected. Supporting experiments that were performed under identical conditions except for the use of Pu-242 rather than Pu-239 did not result in the reduction of Pu(VI) to Pu(V). The overall effect of radiolytic processes, when viewed in the context of all speciation pathways for the total subsurface system, is however not directly addressed by the results of our experiments since our starting point was Pu(VI), not Pu(IV) which is the most likely oxidation state of plutonium in emplaced TRU waste where plutonium oxide is the most likely form of plutonium.

3.2 Effect of MgO on the stability of Pu(VI)

The MgO experiments performed are described in Table 1. The concentration of plutonium as a function of time in these experiments is summarized in Table 4 and shown in Fig. 2. The presence of MgO resulted in a relatively small but significant decrease in plutonium concentrations. MgO was only added to experiments Pu-E8 and Pu-E10 which are the carbonate containing experiments performed in ERDA-6 brine at pC_{H^+} 8 and 10 respectively. Carbonate removal, which would presumably lead to the destabilization of the
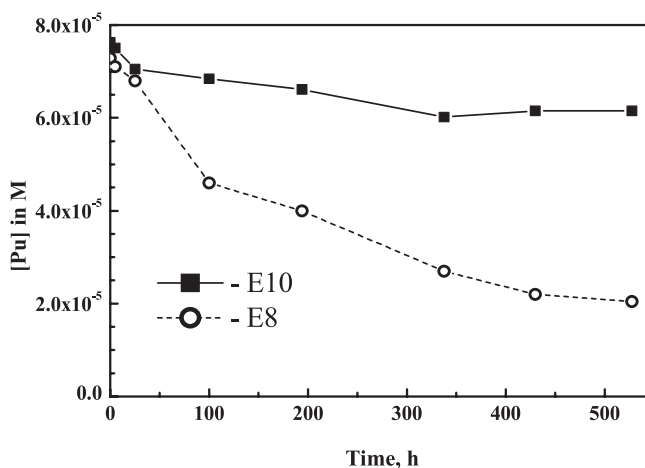

Fig. 2. Concentration of plutonium as a function of time in the presence of excess MgO for experiments Pu-E8 (top curve) and Pu-E10 (bottom curve).

Table 4. Concentration of plutonium as a function of time for the iron coupon, added Fe^{2+}, and MgO interaction studies.

Experiment Description	[Pu] in 20 nm-filtered samples as a function of time (M) – uncertainty is ±5%						
Time (h), Fe coupon	Initial	3.1 h	22.1 h	46.0 h	121.3 h	214.6 h	455.9 h
G5-FE	7.11×10^{-5}	4.55×10^{-5}	6.29×10^{-6}	4.91×10^{-6}	3.87×10^{-6}	1.68×10^{-6}	7.00×10^{-8}
G7-FE	7.99×10^{-5}	5.93×10^{-5}	1.35×10^{-6}	1.11×10^{-6}	6.84×10^{-7}	3.22×10^{-7}	5.07×10^{-8}
E8-FE	7.29×10^{-5}	6.52×10^{-5}	3.84×10^{-5}	8.14×10^{-6}	1.59×10^{-6}	5.84×10^{-7}	9.02×10^{-8}
E10-FE	7.63×10^{-5}	6.26×10^{-5}	3.49×10^{-5}	2.09×10^{-5}	2.77×10^{-7}	1.13×10^{-7}	1.11×10^{-7}
E10NC-FE	7.39×10^{-5}	7.35×10^{-5}	5.95×10^{-5}	4.72×10^{-5}	2.12×10^{-5}	1.31×10^{-8}	6.87×10^{-9}
Time (h), added Fe^{2+}	Initial	2.1 h	5.2 h	25.1 h	49.7 h	121.4 h	216.8 h
G5-FE2	6.77×10^{-5}	4.24×10^{-5}	3.48×10^{-5}	2.82×10^{-5}	3.02×10^{-5}	2.17×10^{-5}	2.22×10^{-5}
G7-FE2	8.40×10^{-5}	8.90×10^{-7}	5.85×10^{-7}	3.60×10^{-7}	2.52×10^{-7}	1.54×10^{-7}	1.16×10^{-7}
E8-FE2	6.88×10^{-5}	5.50×10^{-7}	2.78×10^{-7}	1.42×10^{-7}	1.04×10^{-7}	1.17×10^{-7}	NA
E10-FE2	7.47×10^{-5}	5.37×10^{-7}	2.27×10^{-7}	1.31×10^{-7}	1.41×10^{-7}	1.35×10^{-7}	NA
E10NC-FE2	7.55×10^{-5}	2.83×10^{-8}	9.98×10^{-9}	4.69×10^{-8}	1.79×10^{-8}	1.05×10^{-8}	NA
Time (h), added MgO	Initial	5.0 h	25.3 h	100.3 h	193.8 h	337.7 h	527.8 h
E8-MGO	7.29×10^{-5}	7.08×10^{-5}	6.74×10^{-5}	4.60×10^{-5}	3.96×10^{-5}	2.70×10^{-5}	2.04×10^{-5}
E10-MGO	7.63×10^{-5}	7.50×10^{-5}	7.05×10^{-5}	6.84×10^{-5}	6.61×10^{-5}	6.02×10^{-5}	6.15×10^{-5}

NA: not analyzed.

Pu-carbonate complex, did not occur in the timeframe of these experiments. For this reason, the observed decrease in plutonium concentration cannot be attributed to the now well-established, but longer-term, reactivity of MgO with carbonate. Only Pu(VI) carbonate species were noted in solution and there was no spectral evidence for reduction.

The MgO used in these experiments was pure reagent grade MgO with essentially no iron content. This is an important difference from the MgO found in nature, and currently used as an engineered barrier in the WIPP, which can contain a significant amount of iron (Premier MgO used earlier in WIPP had $\sim$ 1% iron, currently Martin Marietta MgO has significantly less than this). The lack of reduction, in our experiments, contrasts with the results using real-system MgO, where the reduction of Pu(VI), presumably by the iron in MgO, was observed [18].

The best explanation of the observed loss of Pu observed in our results is that the Pu(VI) is sorbing onto the MgO material or that the MgO is facilitating the precipitation of Pu(VI) phases. This is reasonable given the high MgO surface area present and available in these experiments and explains the greater loss of plutonium at pC_{H+} 8 where a less stable carbonate complex would be expected. These explanations are however mainly speculative and are based on the absence of spectral evidence for Pu(V) and/or Pu(IV) species and the unlikelihood that MgO will function as a reducing agent. Further study of MgO effects on plutonium speciation and mobility, at longer times, is needed to further establish the key mechanisms of interaction.

3.3 Reduction of Pu(VI) by zero-valent iron (steel)

The presence of a zero-valent iron (steel) coupon, under anoxic conditions, led to the reduction of plutonium(VI) to plutonium(IV). This, as shown in Fig. 3 and summarized in Table 4, led to as much as four orders of magnitude decrease in the plutonium concentration and the precipitation of plutonium phases from the various brines. As evident in Fig. 3, plutonium in G-Seep brine was most rapidly removed. Carbonate complexation at both pC_{H+} 8 and 10 resulted in slower decrease in the plutonium concentration but, ultimately, similar total plutonium concentrations
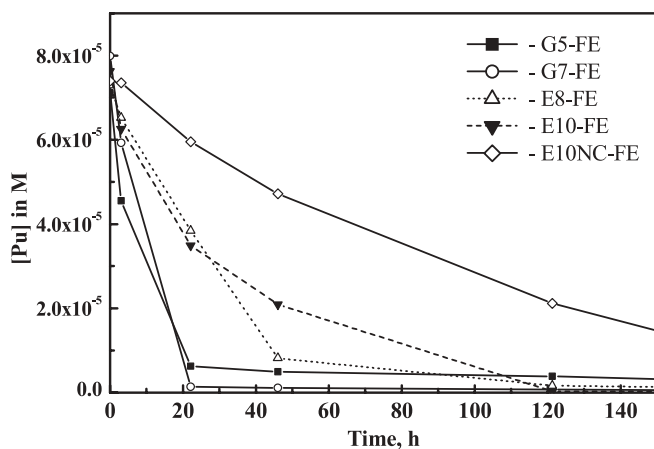
were obtained. The plutonium species in the carbonate-free pC_{H+} 10 ERDA-6 experiment was removed from solution at the slowest rate. Given the wide range of pH, the variety of plutonium species present, and the competition between sorption, redox and precipitation in the experiments, it is difficult to establish the details of the mechanism for these observed effects.

The plutonium precipitates and iron coupons used were recovered and encapsulated in a polystyrene matrix under anoxic conditions for XANES/EXAFS analysis. Typically $\sim$ 30%–40% of the reduced plutonium in these experiments was on the metal surface. XANES analysis of the plutonium precipitate (see Fig. 4) and the plutonium associated with the iron surface matched the edge position and shape of our Pu(IV)O$_2$ reference phase. This confirmed that reduction had taken place, but, generally speaking, XANES analysis is not a very precise technique for establishing oxidation state distribution so it is not possible to preclude
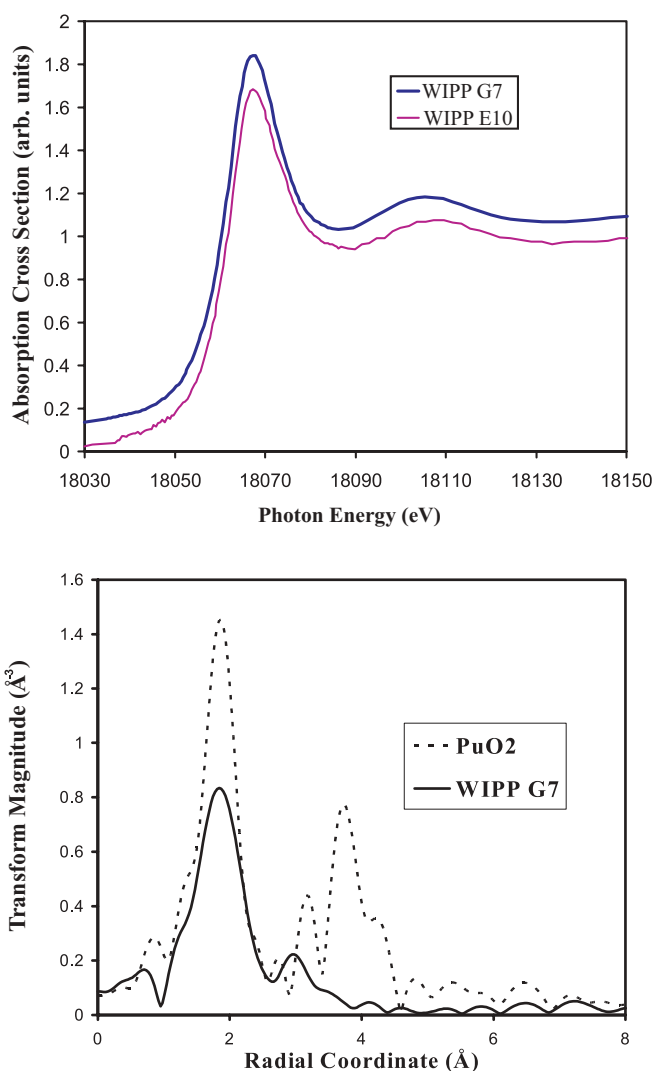

Fig. 4. XANES spectra (top) of the precipitates from the G7 and E10 experiments after the addition of zero valent iron coupons. The spectra are purposefully offset and match the edge position of the Pu(IV)O$_2$ standard used confirming that reduction from Pu(VI) to Pu(IV) had taken place. EXAFs (bottom), in radial space, of plutonium precipitates collected from the pC_{H+} 7 WIPP experiments containing iron and a PuO$_2$ reference. There is agreement in the Pu−O bond length, but much greater disorder in the brine precipitate plutonium phase.

Fig. 3. The concentration of plutonium as a function of time in the presence of zero-valent iron (as steel coupons). The overall rate of reduction was G7 $\approx$ G5 > E8 $\approx$ E10 − NC.

the presence of small amounts of Pu(III) ($\sim 10\%$ or less) in our samples. The EXAFS analysis, in radial space, of the precipitate obtained at pC_{H+} 7 is also shown in Fig. 4 and compared to the spectrum of our plutonium oxide standard. Although there is a good match in Pu−O bond lengths there is much greater disorder in the WIPP sample, which is indicative of the amorphous nature of the brine precipitate.

The concentration effects, XANES analysis, and consistency of the resulting concentrations with the calculated Pu(IV) concentrations combine to show that in the presence of zero-valent iron, all the Pu(VI) species are reduced to Pu(IV) leading to precipitation of Pu from solution. This occurred even though these Pu-239 experiments had equilibrated for $\sim$ two years meaning there was sufficient time for radiolytic products to have reached steady state.

The plutonium oxidation state in the aqueous phase in our experiments was not directly determined and is less certain. The final empirical steady state plutonium concentrations we measured, however, are most consistent with what is expected for Pu(IV) and Pu(III) species in the presence of milli-molar concentrations of carbonate. Additionally, the low plutonium concentration observed at $pC_{H+} = 5$, along with the strong dependence of the plutonium concentration on the presence of carbonate, qualitatively point towards a predominantly Pu(IV) aqueous species. The likely predominance of the Pu(IV) oxidation state in our experiments does not agree with thermodynamic predictions for the predominance of Pu(III) species in a hydrogen-iron anoxic system but is reasonable given the radiolysis effects (*i.e.*, buildup of oxy-chlorides) that may be present in these long-term studies. Our data suggest that Pu(IV) precipitation is functioning as a "sink" for plutonium as the plutonium is reduced by the metal. Essentially, under the conditions of our experiments Pu(IV) precipitation is proceeding at a faster rate than the further reduction of Pu(IV) to Pu(III). The role of Pu(III) species in these iron-rich anoxic systems is the subject of further and ongoing experimental work.

3.4 Effect of Fe^{2+} on the stability of Pu(VI) in brine

The addition of Fe^{2+}, as a chloride complex, to the various brines was done under anoxic conditions (see Tables 1 and 4). This led to the rapid reduction (see Fig. 5) of plutonium concentrations in all cases but experiment G5 which corresponds to G-Seep brine at pC_{H+} 5. An absorption spectrum of the plutonium in this experiment showed that the plutonium remaining in solution was PuO$_2$$^+$. These overall results are difficult to interpret due to the complexity of the Fe^{2+} system under the conditions of our experiments in the simulated brines. Overall, the extent of reduction was significantly less (by a factor of 10–100) than that observed for zero-valent steel. It is likely that the difference observed at pC_{H+} 5 was mostly due to the difference in the speciation of the iron rather than the plutonium chemistry at that pH – but this needs further study.

4. Summary of conclusions

Plutonium (VI), when no reducing agent was present, was stable under all conditions investigated in WIPP brine. Under these conditions, little/no precipitation of the pluto-
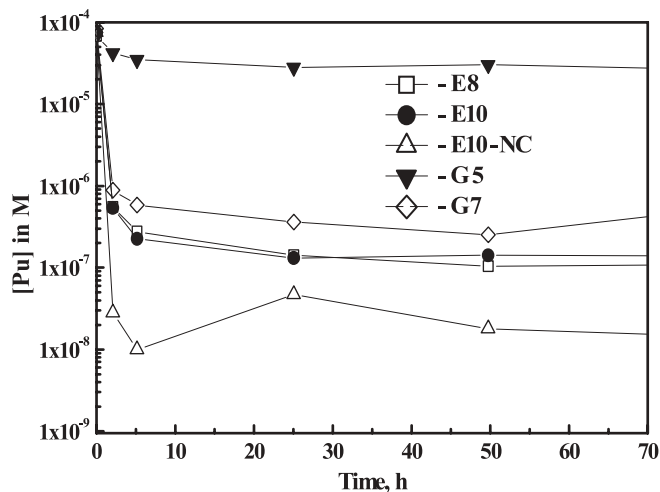

Fig. 5. Effect of added Fe^{2+} on the stability of Pu(VI) in brine. Total plutonium concentrations were reduced by four orders of magnitude with the exception of experiment G5 which was conducted at pC_{H+} 5 in G-seep brine where aqueous Pu(V) species persisted.

nium was noted. This persisted for the two-year duration of the experiments performed and was confirmed by absorption spectra of 20 nm filtered solutions where hydroxy-chloro and carbonato species were observed.

The addition of zero-valent iron coupons or aqueous Fe^{2+} rapidly destabilized Pu(VI) under most conditions investigated. The presence of MgO, which was not expected to be redox active, led to a slow loss of plutonium from solution. This was tentatively attributed to the sorption of plutonium(VI) and/or the facilitation of its precipitation. When iron was added, either as zero-valent steel coupons or an Fe^{2+} chloride complex, the plutonium concentrations were reduced by 2–4 orders of magnitude in all but one case. The one exception was at pC_{H+} 5 when Fe^{2+} was added where reduction to Pu(V) was observed. XANES analysis of selected plutonium precipitates and plutonium sorbed onto the steel surface confirmed this to be a predominantly Pu(IV) phase. This establishes that reduction had taken place and suggests that Pu(IV) species predominate in irradiated anoxic systems when iron is present.

References

1. Runde, W.: The chemical interactions of actinides in the environment. Los Alamos Sci. **26**, 330 (1994).
2. Nitsche, H., Roberts, K., Xi, R., Prussin, T., Becraft, K., Al Mahamid, I., Silber, H. B., Carpenter, S. A., Gatti, R. C., Novak, C. F.: Long term plutonium solubility and speciation studies in a synthetic brine. Radiochim. Acta **66/67**, 3 (1994).

3. Duff, M. C. , Hunter, D. B., Triay, I. R., Bertsch, P. M., Reed, D. T., Sutton, S. R., Shea-McCarthy, G., Kitten, J., Eng, P., Chipera, S. J., Vaniman, D. T.: Mineral associations and average oxidation states of sorbed Pu on tuff. Environ. Sci. Technol. **33**, 2163 (1999).

4. Villarreal, R., Bergquist, J. M., Leonard, S. L.: The actinide Source-Term Waste Test Program (STTP): Final Report, 3 volumes: LA-UR-01-6822, LA-UR-01-6912 and LA-UR-01-6913 (2001).

5. Pashalidis, I., Kim, J. I., Lierse, Ch., Sullivan, J.: The chemistry of Pu in concentrated aqueous NaCl solution: Effects of alpha self-radiolysis and the interaction between hypochlorite and dioxoplutonium(VI). Radiochim. Acta **60**, 99 (1993).

6. Reed, D. T., Aase, S. B., Wygmans, D., Banaszak, J. E.: The reduction of Np(VI) and Pu(VI) by organic chelating agents. Radiochim. Acta **82**, 109 (1998).

7. Zeh, P., Kim, J. I., Marquardt, C. M., Artinger, R.: The reduction of Np(V) in groundwater rrich in humic substances. Radiochim. Acta **87**, 23 (1999).

8. Banaszak, J. E., Reed, D. T., Rittmann, B. E.: Subsurface interactions of actinide species and microorganisms: Implications for the bioremediation of actinide-organic mixtures. J. Radioanal. Nucl. Chem. **241**, 385 (1999).

9. Rittmann, B. E., Banaszak, J. E., Reed, D. T.: Reduction of Np(V) and precipitation of Np(VI) by an anaerobic microbial consortium. Biodegradation **13**(**5**), 329 (2002).

10. U.S. DOE.: Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant, Carlsbad, NM. U.S. Department of Energy Carlsbad Area office, Vol. 1–21 (1996).

11. U.S. DOE.: Title 40 CFR Part 191 Compliance Recertification Application for the Waste Isolation Pilot Plant, DOE/WIPP 2004-3231, Carlsbad, NM: U.S. Department of Energy Carlsbad Field Office, Vol. 1–8 (2004).

12. Reed, D. T., Aase, S. B., Kropf, A. J., Conca, J.: Reduction of plutonium(VI) species in brine. In plutonium futures – The science conference transactions. (Jarvinen, G. D., ed.) Am. Inst. Phys. 372 (2003).

13. Farrell J., Bostick, W. D., Jarabeck, R. J., Fiedor, J. N.: Uranium removal from ground water using zero valent iron media. Ground Water **37**(**4**), 618 (1999).

14. Xia, Y., Rao, L., Rai, D., Felmy, A. R.: Determining the distribution of Pu, Np and U oxidation states in dilute NaCl and synthetic brine solutions. J. Radioanal. Nucl. Chem. **250**, 27 (2001).

15. Reed, D. T., Okajima, S.: Stability and speciation of plutonium(VI) in WIPP brine. Radiochim. Acta **66**/**67**, 95 (1994).

16. Rai, D., Moore, D. A., Felmy, A. R., Choppin, G. R., Moore R. C.: Thermodynamics of the PuO_2^+-Na^+-OH^--Cl^--ClO_4^--H_2O system: use of NpO_2^+ Pitzer parameters for PuO_2^+. Radiochim. Acta **89**, 491 (2001).

17. Felmy, A. R., Rai, D., Schramke, J. A., Ryay J. L.: The solubility of plutonium hydroxide in dilute solution and in high-ionic strength chloride brines. Radiochim. Acta **48**, 29 (1989).

18. Lu, N., Conca, J.: Plutonium-239 in synthetic brines after equilibrartion with magnesium oxide backfill. In plutonium futures – the science conference transactions. (Jarvinen, G. D., ed.) Am. Inst. Phys. **673**, 302 (2003).