Stability of Plutonium(VI) in Selected WIPP Brines

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Abstract

The redox stability of plutonium(VI) in WIPP brine was investigated by monitoring the oxidation state as a function of time using a combination of absorption spectrometry, radiochemical counting and filtration. Studies were performed with Pu-239 and Pu-238 in four WIPP brines at concentrations between 10^{-3} and 10^{-8} M for durations as long as two years. Two synthetic brines, Brine A and ERDA-6, and two brines collected in the WIPP underground, DH-36 and G-Seep, were used. The stability of Pu(VI) depended on the brine composition and the speciation of the plutonium in that brine. When carbonate was present, a stable Pu(VI)-carbonate complex was observed. In the absence of carbonate, Pu(VI) hydrolytic species predominate. These species had a wide range of stability in the brines investigated. The reported results will help define the speciation of plutonium in WIPP brine and its potential for migration.

Introduction

Herein, we report the results of work that was done in support of gas generation experiments with Pu-spiked brines performed for the Waste Isolation Pilot Plant (WIPP) [1−4]. It is important to note that the primary objective of these experiments was to establish the stability of plutonium in solution rather than its solubility in WIPP brine. Qualitative information on the likely speciation of plutonium in the systems we studied is also reported. Both the speciation and stability data are limited and should be interpreted in the context of all the work being sponsored by the WIPP to address the issue of plutonium solubility.

The WIPP, located in the Salado bedded salt formation in southeastern New Mexico in the northern portion of the Delaware Basin, is being investigated as a site for final disposal of transuranic (TRU) waste [5, 6]. The predominant actinide in TRU waste will be plutonium-239 which is present at levels of up to 10 grams per waste drum. The most likely scenarios leading to plutonium migration from the WIPP are human intrusion and brine inundation which may mobilize the plutonium as an aqueous species. The speciation and solubility of plutonium under this latter scenario, therefore, are potentially important factors in evaluating the long-term performance of the WIPP.

The key parameters that define the speciation and solubility of plutonium in WIPP brines are redox con-

ditions, pH, carbonate concentration, organics present, degree of aggregation, and inorganic complexation. The operational pH (pH_{OP}) of all four WIPP brines investigated was typically in the range of pH = 6 to 7. This was measured by a Ross electrode and uncorrected for ionic strength. The actual pH in these systems is approximately 0.5 to 1 pH unit higher than we measured when corrected for ionic strength [7, 8]. In this pH range, Pu(VI) is readily hydrolyzed in the absence of strong complexants. Of the anions present in WIPP brines (e.g., halides, carbonate/bicarbonate, and sulfate), only the carbonate/bicarbonate species are expected to be important. The formation constants [9, 10] for these species are not well established in dilute systems and are less well-defined in high-ionic-strength media. Spectra obtained in our laboratory relevant to Pu(VI) speciation in WIPP brine are shown in Figure 1 and are consistent with those reported elsewhere [10−13].

Experimental

We established the redox stability of Pu(VI) in WIPP brine by monitoring the oxidation state as a function of time using absorption spectrometry. Studies were performed with $\sim 10^{-3}$, 10^{-4}, 10^{-6}, and 10^{-8} M Pu(VI) in four WIPP brines. Two of these were synthetic brines designated Brine A and ERDA-6. The other two were brines collected in the WIPP underground designated DH-36 and G-Seep. The composition of these brines is given in Table 1.

Plutonium-239, >99% isotopic purity, was received from Oak Ridge National Laboratory and oxidized to be VI state in 50 mg quantities by taking to near-dryness in perchloric acid. The Pu(VI) was dissolved in triple-distilled water and analyzed for oxidation-state purity using absorption spectrometry. We used the absorption at 622 nm with $\varepsilon = 7.5 \, \mathrm{M^{-1} \, cm^{-1}}$ [13] to estimate the plutonium concentration and establish the dilution sequence needed to prepare a solution with the desired plutonium concentration in the WIPP brine.

The pH_{OP} of the stock solution prepared in this way was typically about 1. This was adjusted to a near-neutral pH_{OP} to match the pH_{OP} of the brine, by adding sodium hydroxide. This solution was sequentially diluted twice into the brine of interest to minimize change in the concentration of the bulk constituents of the brine. After each dilution, the solution was checked for evidence of precipitation. This twice-
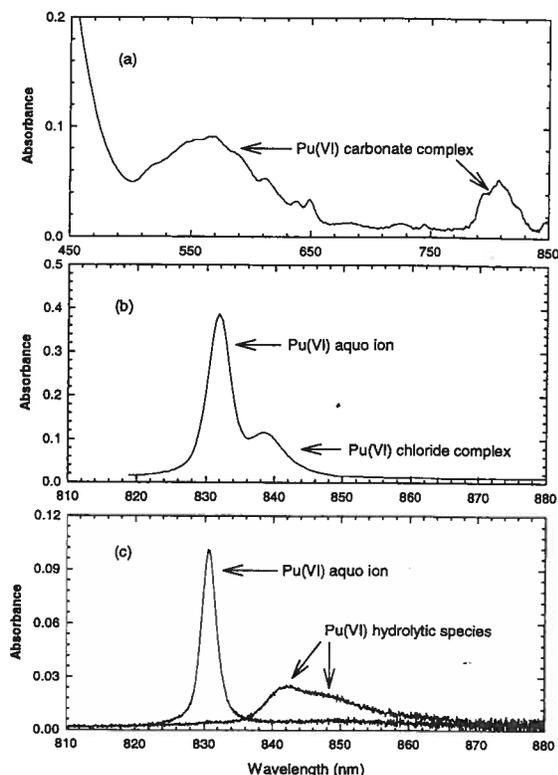
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Fig. 1. Absorption spectra of Pu(VI) species relevant to WIPP brine: (a) 0.0029 M Pu(VI) in 0.01 M carbonate at pH_{OP} = 6.9, (b) Pu(VI) in presence of chloride at pH_{OP} = 3, (c) 2×10^{-4} M Pu(VI) aquo ion (pH_{OP} = 2.8) and hydrolytic species (pH_{OP} = 6.9).

Table 1. Composition of the WIPP brines used in the Pu(VI) stability studies

Element, species, or property	Concentration (M)			
	[1]Brine A	[1]ERDA-6	[2]DH-36	[2]G-Seep
Cl	5.38	4.64	5.37	5.07
SO_4^{2-}	0.044	0.167	0.173	0.297
B	0.020	0.063	0.136	0.14
CO_3^{2-}/HCO_3^-	0.0114	0	<0.00007	<0.00008
Br	0.0051	0.011	0.018	0.017
Na	1.83	4.85	3.67	4.18
K	0.767	0.097	0.471	0.338
Mg	1.44	0.019	0.816	0.612
Ca	0.015	0.012	0.0096	0.0077
[3]pH_{OP}	6.3	6.2	5.94	6.14

[1] Based on recipe provided by the WIPP.

[2] As-received analysis of brine collected underground at the WIPP.

[3] Obtained using a combination Ross electrode and uncorrected for ionic strength.

diluted Pu-spiked brine typically had a plutonium concentration of $\sim 10^{-3}$ M and corresponds to the 2×10^{-3} M solutions identified in Table 2. Additional brine was added to a final volume of 30 to 1000 ml to generate samples with lower plutonium concentra-

tions. These solutions were equilibrated for 3−7 days before taking a sample for alpha scintillation counting. This was done with a Packard Model 2050 alpha scintillation counter by adding a small aliquot of the Pu-spiked brine to Ultima-Gold cocktail and comparing the results against a series of plutonium stock samples prepared in the same way from NIST-traceable plutonium standards. The scintillation-counting data were within 10% of the predicted plutonium concentration based on the dilution sequence utilized.

The two brines collected underground at the WIPP were DH-36 and G-Seep. These had been collected by Sandia National Laboratories (WIPP/SNL), stored in 1 Liter bottles, and subsequently shipped to Argonne. The twenty 1-Liter bottles received for each brine were opened and combined into a single 5-Gallon (18.9 l) polyethylene jug. This jug had been pre-rinsed with high-purity water and two liters of the groundwater. Prior to use, the groundwater in the jug was stirred and coarse filtered, using a glass frit, in room air. There was no attempt to control P_{CO_2} throughout the handling, filtration, and addition of the brines to the vessels. We confirmed that the groundwaters did not initially contain significant levels of carbonate by analyzing the head space in the jug above the brine for carbon dioxide. All groundwaters were stored in sealed vessels in the dark at room temperature (21±2 °C).

Approximately 3 ml of the Pu-spiked brine was placed in a 1×1-cm gas-tight quartz cuvette for spectrometric analysis. These samples were also kept in the dark at room temperatures (21±2 °C) and periodically analyzed to monitor changes in the absorption spectrum. Absorption spectra were obtained with either a Hitachi model 340 or a Varian CARY-5 spectrometer and recorded digitally for analysis. On the Hitachi spectrometer, visible and NIR spectra were obtained independently. This is denoted in the figures by a dashed line. The Pu(VI) absorption in the high concentration plutonium samples (10^{-3} M), had an optical density greater than 0.1. The reference for these spectra was the same brine used to make up the plutonium-containing samples in a similar cuvette. For the $\sim 10^{-4}$ M Pu-spiked brines, where the absorbance was low, both reference and sample spectrum were taken in the same cuvette to minimize cell-to-cell differences in absorbance.

Results and discussion

The stability experiments performed are listed in Table 2. Also included are the corresponding alpha-scintillation counting data. We report data that were obtained over a period of up to 26 months. Some of these experiments, however, are still ongoing.

Stability of Pu(VI) in Brine A

The majority of the stability experiments were performed in Brine A which was the only brine investigated

Table 2. Summary of stability experiments and related counting data. Uncertainty is ±10%

WIPP brine	Experiment designation	Nominal [Pu], M	Experiment duration, months	[Pu], M	
				Initial	Final
Brine A	Stock	0.0023	12	ND	ND
	GG-B1-41	10^{-4}	26	3.4×10^{-4}	ND
	GG-B1-42	10^{-4}	26	2.8×10^{-4}	2.7×10^{-4}
	GG-B1-61	10^{-6}	6	6.3×10^{-7}	7×10^{-7}
	GG-B1-62	10^{-6}	6	5.4×10^{-7}	7×10^{-7}
	GG-B1-81	10^{-8}	6	6.7×10^{-9}	6.7×10^{-9}
	GG-B1-82	10^{-8}	6	7.1×10^{-9}	7.5×10^{-9}
	[b]GG-38-61	10^{-6}	4.5	7.8×10^{-7}	7.7×10^{-7}
	[b]GG-38-62	10^{-6}	4.5	7.7×10^{-7}	7.2×10^{-7}
	[b]GG-38-81	10^{-8}	4.5	9.0×10^{-9}	8.5×10^{-9}
	[b]GG-38-82	10^{-8}	4.5	8.5×10^{-9}	8.1×10^{-9}
ERDA-6	GG-B4-41	10^{-4}	8	1.1×10^{-4}	0.86×10^{-4}
	GG-B4-42	10^{-4}	8	1.9×10^{-4}	1.1×10^{-4}
DH-36	Stock	10^{-3}	12	0.002	ND
	GG-B3-41	10^{-4}	4	0.99×10^{-4}	0.64×10^{-4}
	GG-B3-42	10^{-4}	4	1.4×10^{-4}	0.70×10^{-4}
G-Seep	Stock	10^{-3}	12	0.002	ND
	GG-B2-41	10^{-4}	4	1.1×10^{-4}	0.44×10^{-4}
	GG-B2-42	10^{-4}	4	1.4×10^{-4}	0.57×10^{-4}

[a] By alpha scintillation counting.
[b] Pu isotope was Pu-238 introduced in the III oxidation state.
ND — not determined.

that had significant levels of carbonate in solution. Spectra and counting data were obtained when the total plutonium concentration exceeded 10^{-4} M. When the concentration was on the order of 10^{-6} M or less, only counting data were obtained, since the absorbance was too low to detect.

Based on the counting data, there was no significant decrease in the plutonium concentration as a function of time for all the plutonium isotopes and concentrations investigated. Filtering the solution through 0.2 µm filters did not affect the total concentration measured.

Absorption spectra for the carbonate complex in Brine A are shown, as a function of time, in Figure 2. At plutonium concentrations greater than 10^{-4} M, a plutonium(VI)-carbonate complex was observed that was stable with time. This solution was also filtered through a 0.2 µm filter and reanalyzed spectrometrically. No change in the spectrum was observed. There was no spectral evidence for Pu(V) or Pu(IV) carbonate species although we cannot preclude the possibility of their existence at low concentrations (<10% of the total plutonium).

The absorption spectrum obtained in Brine A is most similar to that obtained for the Pu(VI) carbonate species (see Figure 1). It is characterized by a blue-shifted absorption band at 806 nm. The apparent extinction coefficient for the species we have observed was approximately 40 M^{-1} cm^{-1} which is comparable to that published for the carbonate complex [11]. Some evidence of Pu(VI) hydrolytic species can be seen in the higher resolution CARY-5 spectrum (Fig. 2c). It is not surprising that a carbonate species is predominant

in Brine A since this brine contains 0.011 M sodium bicarbonate and the pH$_{OP}$ of the brine is greater than 7.

Based on our data, we are proposing that the Pu(VI) species in Brine A is primarily a carbonate complex. Detailed library spectra, however, do not exist that would permit a more specific species assignment. Both Pu(VI) in Brine A and Pu(VI) in the carbonate/bicarbonate system has a broad absorption at 570 nm. In the 800−850 nm regime however, significant differences are apparent. The full-width half-height of the 806 nm absorption is 10 nm for Brine A compared with 30 nm in the carbonate/bicarbonate system. In addition to this, there is greater complexity in the band structure in the bicarbonate/carbonate sample.

We believe that the best explanation for the observed stability of the Pu(VI)-carbonate species is the presence of carbonate rather that radiolysis. In the absence of carbonate (see later discussions for ERDA-6 brine and the higher concentration samples for G-Seep and DH-36 brines), we observed autoreduction of Pu(VI) to a Pu(V/VI) mixture in solutions with comparable activity (i.e. the same dose rate). This phenomena was also reported elsewhere [14] in brine systems. Here there was a relatively rapid reduction of Pu(VI) due to radiolysis followed by a slower re-oxidation to Pu(VI) that was attributed to the radiolytic formation of oxygen chlorides in the brine. This initial reduction was not observed in our experiments when carbonate was present. The stability of the Pu(VI) carbonate complex in WIPP brine, however, is consistent with theoretical predictions [15] and experimental results
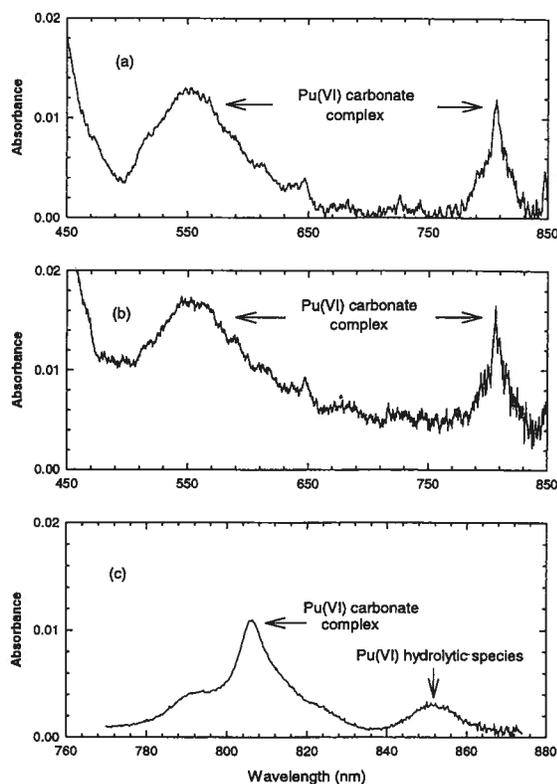
Fig. 2. Absorption spectra of 3×10^{-4} M Pu(VI) in WIPP Brine A at (a) 0, (b) 475, and (c) 945 days. Spectra a and b were obtained on the Hitachi model 340 spectrometer and spectrum c was obtained using the Varian CARY-5 spectrometer (note different wavelength scale).

Fig. 3. Absorption spectra of 1.1×10^{-4} M Pu(VI) in ERDA-6 brine at (a) 6, and (b) 294 days after sample preparation.

[14] reported elsewhere. It has also been partly corroborated by results reported by others in the WIPP Project [16].

Stability of Pu(VI) in ERDA-6 Brine

The stability and speciation of Pu(VI) in ERDA-6 brine was significantly different than that observed in Brine A because of the absence of carbonate and bicarbonate. The absorption spectra of Pu(VI) in ERDA-6, as a function of time, are shown in Figure 3. The sample was analyzed spectroscopically at 6, 77, 280 and 294 days after preparation.

The absorption spectra shown in Figure 3 are most similar to those for the hydrolytic species (see Figure 1). At this pH, the Pu(VI)-chloride complex would not be expected to successfully compete with hydrolysis [17]. The best interpretation of the 845 nm band is that it corresponds to a Pu(VI) species that is predominantly hydrolytic in nature. Further detailed studies are, however, needed to more fully evaluate the effect of ionic strength on band structure.

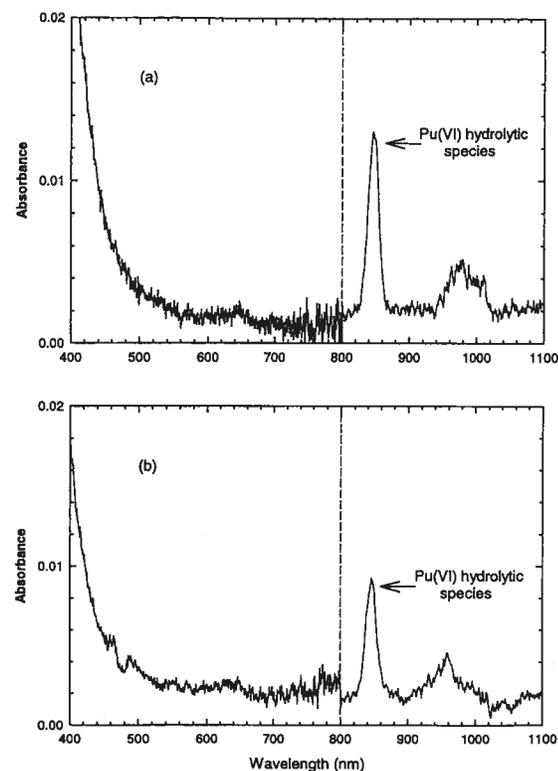The redox stability of the Pu(VI)-hydrolytic species observed in ERDA-6 was less than, but comparable to, that observed for the Pu(VI)-carbonate complex in Brine A. There is a loss of approximately 25—30% of the absorbance at 845 nm when the 6-day and 295-day spectra are compared. The total concentration of plutonium in this brine remained constant in both unfiltered and 0.2-μ filtered solutions, based on alpha-scintillation counting data. Reduction to Pu(V) is postulated, but 3×10^{-5} M Pu(V) would not be observable spectroscopically ($\varepsilon = 19$ M^{-1}cm^{-1} at 569 nm).

Stability of Pu(VI) in DH-36 Brine

The samples taken from the gas generation experiments GG-B3-41 and GG-B3-42 were spectroscopically analyzed to evaluate the stability of Pu(VI) in DH-36 brine. There was no longer any spectroscopic evidence for Pu(VI) six days after sample preparation. There was, however, a small absorption (OD = 0.0015) apparent at 569 nm that corresponds to Pu(V). This would account for approximately 75% of the plutonium initially present in solution. In spectra obtained at 280 and 295 days after sample preparation, the absorption spectrum was featureless. There was no evidence for either Pu(V) or Pu(VI). This suggests that reduction of the plutonium had proceeded to lower oxidation states of plutonium where polymerization would be expected. The speciation of the plutonium species remaining in solution was not established.
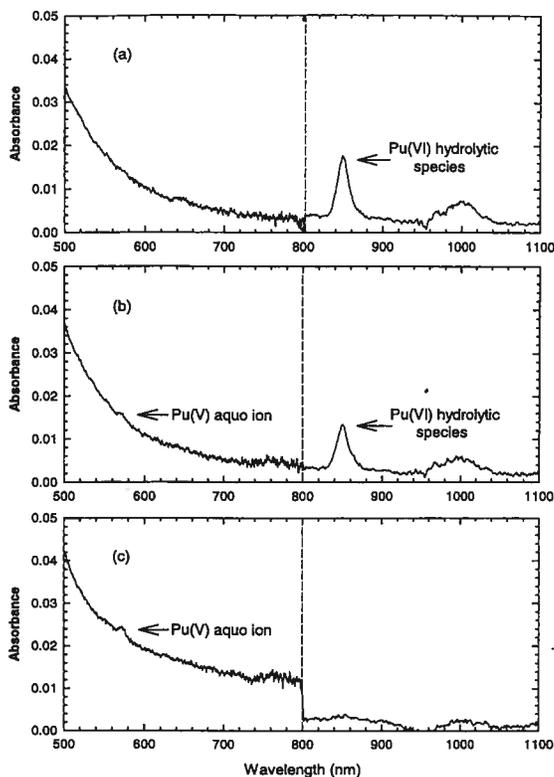
Fig. 4. Absorption spectra of $\sim 10^{-4}$ M Pu(VI) in DH-36 brine at (a) time = 0, (b) after 2 hrs, and (c) at 3 days after sample preparation.

To determine the rate at which Pu(VI) was reduced in DH-36 brine, a new sample was prepared and spectroscopically monitored. These time-dependent spectra are shown in Figure 4. The initial concentration of plutonium was 1.9×10^{-4} M and the pH_{OP} was 6.1. Initially, the 845-nm band characteristic of the Pu(VI) hydrolytic species was observed. Two hours after sample preparation approximately 25% of the Pu(VI) was reduced to Pu(V). Three days after sample preparation, there was no spectroscopic evidence for Pu(VI), however, an increase in the Pu(V) absorption was observed.

At higher plutonium concentrations (0.0035 M), both filtered and unfiltered solutions of Pu(VI) in DH-36 brine were monitored spectroscopically for 337 days. For both solutions, the absorption spectrum was most similar to those of the Pu(VI) hydrolytic species and ERDA-6 brine. There were no significant differences noted between the filtered and unfiltered samples.

The long-term redox stability of Pu(VI) at this higher plutonium concentration was much greater than that noted at concentrations an order of magnitude lower. After 337 days, the spectrum obtained indicated that there were approximately equimolar concentrations of Pu(V) and Pu(VI) in solution, estimated to be 0.0011 and 0.0014 M respectively. This finding

contrasts with the complete and rapid reduction observed at $\sim 10^{-4}$ M plutonium concentrations. Autoradiolysis at comparable plutonium concentrations resulted in complete conversion of Pu(VI) to Pu(IV) for low ionic strength solutions at pH_{OP} = 3 [13]. The combination of higher pH, high ionic strength, and the radiolytically-induced changes in the brine stabilized the Pu(V/VI) against autoreduction to Pu(IV). This was presumably due to the radiolytic formation of oxygen chlorides in the brine [14].

Although there are a number of questions raised by these results that cannot be fully resolved, there are some observations related to the redox stability and speciation of Pu(VI) in DH-36 that were made. First, the initial speciation of Pu(VI) appears to be a hydrolytic species. This proposed assignment is based on spectral comparisons with Pu(VI) in ERDA-6 and non-complexing medias. This species is rapidly reduced at plutonium concentrations of $\sim 10^{-4}$ M. This reduction is fast relative to autoradiolysis and is caused by a reducing agent in the brine. We could not establish the nature of the reducing agent or the plutonium species generated, although a Pu(IV) aggregate, perhaps a polymeric species, is likely at the near-neutral pH of the brine.

At concentrations of plutonium $>10^{-3}$ M, the predominant species were Pu(V) and hydrolyzed Pu(VI). These oxidation states of plutonium have persisted for a year. The concentration of Pu(VI) and Pu(V) appear to reach steady-state with time.

Stability of Pu(VI) in G-Seep brine

The samples of 10^{-4} M Pu(VI) in G-Seep brine were taken from the gas generation experiments GG-B2-41 and GG-B2-42. The time-dependent spectra are presented in Figure 5. Six days after sample preparation, the dominant species appears to be the Pu(VI) hydrolytic species, with a maximum absorption at 845 nm. The estimated concentration of this species was 4×10^{-5} M, about 40% of the total plutonium initially present in solution. An absorption band at shorter wavelength was also present.

At 77 days, there was no spectral evidence of Pu(VI). After 280 days, there was no absorbance characteristic of dissolved plutonium species. Based on the alpha-scintillation counting results, however, over half the plutonium originally present in solution was still there. The nature of this plutonium species was not established.

As with the DH-36 brine sample, a 0.0035 M Pu(VI) solution in G-Seep brine was prepared. Plutonium solutions for both the filtered and unfiltered brine were monitored the same way. No significant differences were observed between the spectra obtained. At this higher plutonium concentration the hydrolytic species appears to be predominant, with an absorption band at ~ 845 nm. A slow decrease in the concentration of this species was noted with time,
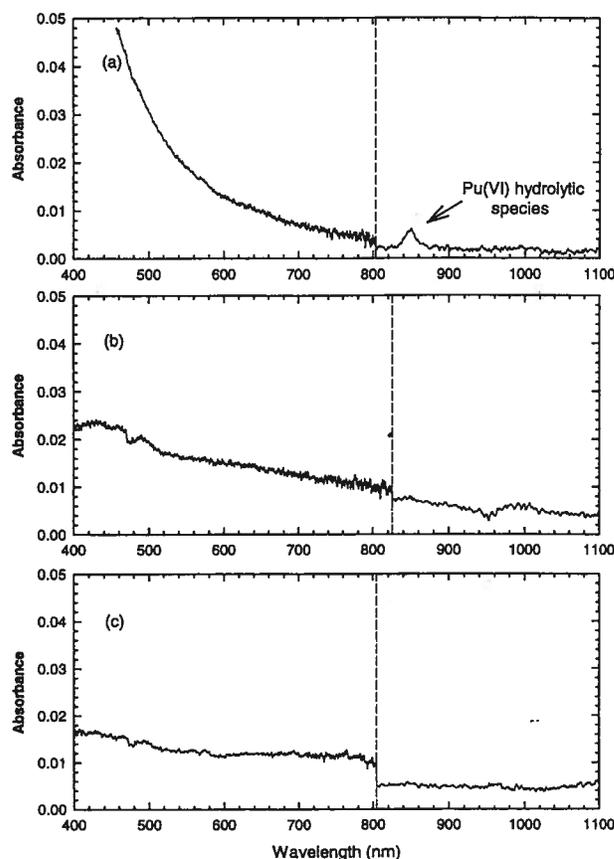
Fig. 5. Absorption spectra of 1.1×10^{-4} M Pu(VI) in G-Seep brine at (a) 6, (b) 77, and (c) 280 days after sample preparation.

along with a corresponding increase in the concentration of Pu(V) at 569 nm. After 337 days, the concentration of the Pu(VI) hydrolytic species was 0.0014 M and the concentration of Pu(V) was 0.0008 M. Additionally, the total plutonium concentration decreased by 40%.

Discussion and summary of observations

Plutonium at concentrations of $\sim 10^{-4}$ M remained in solution in both synthetic brines investigated. In Brine A, a Pu(VI)-carbonate complex was observed that has been stable for over two years. This complex appears to stabilize Pu(VI) towards autoreduction to Pu(V). In ERDA-6, the Pu(VI) species was predominantly hydrolytic in nature and was partly reduced to Pu(V) over the course of a year.

Pu(VI) was significantly less stable in the WIPP brines collected underground. In DH-36, Pu(VI) was rapidly reduced at total Pu concentrations of $\sim 10^{-4}$ M or less. This occurred in the timeframe of a few hours. The reducing agent in this process was not identified. It was likely due to the presence of trace constituents, such as reduced metals or organics, in the groundwater. At plutonium concentrations above 10^{-3} M, Pu(VI) was much more stable in both DH-36 and G-Seep. When reduction occurred in DH-36, most of the plutonium remained in solution as an undefined spe-

cies that did not adsorb strongly in the visible-NIR range. The loss of plutonium was probably due to precipitation of plutonium phases. The absence of absorption bands characteristic of Pu(III, IV, V, VI) for the plutonium remaining in solution suggests that a colloidal or polymeric species may be present. This, however, was not directly established in our work. In G-Seep, the intial species was also predominantly hydrolytic. This was reduced to Pu(V) which was subsequently reduced to an unidentified species that mostly remained in solution.

Finally, it is important to quality these results relative to the conditions expected in the WIPP. Since the Pu(VI) in our studies is introduced at high initial concentrations, we potentially have a radiolysis-dominated system that is more oxidizing than that expected in the WIPP. Reducing agents introduced by waste emplacement itself, such as organic waste, iron etc., will potentially have an important effect of the reduction and/or removal of plutonium. These factors also need to be taken into account to more fully establish the expected speciation and solubility of plutonium in the WIPP.

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