SPECIATION OF Pu(VI) IN NEAR-NEUTRAL TO BASIC
SOLUTIONS VIA SPECTROSCOPY

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ABSTRACT

The high sensitivity technique of laser photoacoustic spectroscopy and optical absorption spectroscopy were utilized to investigate the hydrolysis of Pu(VI) in perchlorate media. Absorption bands attributed to the hydrolysis of Pu(VI) were characterized in the pH = 6-8 regime which is of most interest to the proposed repository site at Yucca Mountain. Evidence was presented that supported the assignment of the polynuclear species (640 nm species) reported previously [1] as $\text{PuO}_3(\text{OH})_5^{+1}$. Some temperature-dependent LPAS spectra are reported. The results obtained were compared to the predicted speciation of the geochemical code EQ3NR.

INTRODUCTION

The hydrolysis of Pu(VI) in the pH region of 6-8 was investigated utilizing the high-sensitivity spectroscopic method of laser photoacoustic spectroscopy (LPAS) and UV-visible-IR absorption spectroscopy. This is a continuation of previous work published [1]. Emphasis of the work reported herein was on higher pH, temperature-dependent speciation and modeling aspects of Pu(VI) speciation. All of these are important considerations in evaluating the performance of the waste package in the proposed high-level waste repository at the Yucca Mountain site.

This work is a continuation of past studies to utilize both laser-induced fluorescence and LPAS [2-5] to investigate radionuclide speciation in groundwater-relevant systems. The application of laser photoacoustic spectroscopy to the study of radionuclide speciation in groundwater systems was first identified by Kim and coworkers [6-8]. In our work, we have developed an LPAS system with a sensitivity of 3×10^{-7} absorption units/cm in the blue-green region of the spectrum, and modified the LPAS cell assembly to obtain LPAS spectra at elevated temperatures.

The role of Pu(VI) in the migration of plutonium in natural systems is uncertain. Its high solubility in natural systems relative to Pu(IV), combined with and the high and well-documented mobility of U(VI) in natural systems suggest, however, that greater importance may need to be placed on its role. An understanding of its environmental chemistry is clearly applicable to system modeling at the source term, where plutonium may be released as Pu(VI) into solution and in environments, such as near-surface groundwaters, where oxidizing conditions may exist.

Hydrolysis data for plutonium species has been obtained elsewhere [9-13] and was reviewed by Baes and Messmer [14]. The UV-visible spectrum of Pu(VI) was first published by Kraus and coworkers [9,13]. This spectrum, in acid medium, consists of sharp peaks due to f-f inner-electron transitions at 622 nm and 833 nm which have been utilized for analytical purposes. In near-neutral to basic solutions plutonyl undergoes hydrolysis forming $(\text{PuO}_2)_m(\text{OH})_n$ complexes. m,n values of (1,1), (2,2), (2,3), (3,5), (4,7), and (1,2) are proposed in the literature. The effect of this complexation on the 833 nm band has been characterized in high concentration samples and results in the formation of bands that are red-shifted with respect to the aquo ion. An analogous trend was observed for the aquo absorption bands in the 600-700 nm region of the spectrum [1] as is shown in Figure 1.

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EXPERIMENTAL APPARATUS AND METHODS

Pu-242 (0.125 g Pu), as the oxide, was originally obtained from Oak Ridge National Laboratory. This was dissolved in nitric acid and taken to dryness, redissolved in 8N nitric acid, and run through a 1 cm by 10 cm column filled with Bio-Rad MP-1 that had been preconditioned with 8N nitric acid solvent. This removed residual Am^{3+} so that accurate counting measurements could be made at low total Pu concentrations.

The eluent was taken to dryness and redissolved in 4N nitric acid and reanalyzed for actinide content. 1 mL of concentrated perchloric acid was added and slowly taken to near-dryness. This oxidized the Pu in the solution to the +6 state. The stock solution was made by dissolving this solution in 25 mL of 0.1M sodium perchlorate and analyzed via UV-visible spectroscopy and scintillation counting methods. No Pu(V) was noted in the spectra taken immediately after sample preparation. Some Pu(V) however grew in over time (<5%). The initial solution had a pH = 1.1 and concentration of 0.0126M.

pH adjustments were made in a glass beaker while bubbling with argon gas to minimize carbon dioxide uptake. The pH was adjusted by adding appropriate quantities of sodium hydroxide solution that had been sparged with argon. Because of the pH instability noted when the pH was decreased, only upward adjustments in pH were made prior to obtaining "equilibrated" optical and LPAS spectra. Equilibration was reached rapidly at pH < 6. As discussed in a later section, the Pu solution was unstable with respect to precipitation at higher pH. Both LPAS and optical spectrometry were performed at room temperature ($21 \pm 1^\circ\text{C}$).

pH measurements were performed using an Orion Research model 8103 Ross combination electrode and an Orion Research model 901 microprocessor ion analyzer meter. The electrode was calibrated against American Scientific Products pH buffers of 4.000 ± 0.002 and 7.000 ± 0.002 . All the UV-visible spectra and near-IR spectra were obtained on a Perkin-Elmer (Hitachi-340) recording spectrophotometer. The LPAS system utilized has been described elsewhere [2,3].

RESULTS AND DISCUSSION

Results were obtained relative to four areas. These are: (1) characterization of the polynuclear hydrolysis product, (2) optical absorption spectra between pH 6 and 8, (3) temperature-dependent spectra at pH = 5.3, and (4) comparison of the observed spectra with the speciation predicted by EQ3NR.

Characterization of the Polynuclear (640 nm) Hydrolysis Product

Evidence supporting the conclusion that the absorption band observed at 640 nm was polynuclear in nature was presented previously [1]. This assignment was based on two qualitative observations: (1) the dependence of the relative concentration of this species on the total concentration of plutonium and (2) the slow kinetics of the reverse hydrolysis reaction associated with this species.

Based on analogy with the UO_2^{2+} system and predictions found in the literature on the PuO_2^{2+} system, the most likely identity of this species was as the 2:2 complex represented as $(\text{PuO}_2)_2(\text{OH})_2$, the 3:5 complex represented as $(\text{PuO}_2)_3(\text{OH})_5$, or a combination of both. Evidence that the species observed was best described as the 3:5 complex is given in this section.

To distinguish between the 2:2 and 3:5 hydrolysis product a back titration experiment was performed. The pH of a 0.0099M PuO_2^{2+} in 0.1M sodium perchlorate was adjusted to pH = 5.6 and let sit for two days. At

this pH, the predominant specie was the 640 nm specie. The spectrum of this solution was obtained and was stable over the time monitored. 70 microliters of 1.7M HCL was added to 11.0 mL of the pH = 5.6 plutonium solution. A 4 mL aliquot of this solution was placed in the absorption cell and monitored over time with the optical spectrometer. When the change in the spectrum appeared to be stable (after 94 h), the pH of the solution was measured to be pH = 4.7.

The optical spectra of the initial pH = 5.6 solution, the final solution (pH = 4.7) and equilibrated solution at pH = 4.7 (obtained by only upward adjustment of pH) are shown in Figure 2. As is evident in this figure, even though no change in the spectrum was not observed for over 24 h, the final solution had still not become equilibrated (i.e. figure 2b and 2c were not the same). The relative concentration of each species observed in the final spectrum was determined based on the absorption of the aquo species. The concentration of the 1:1 complex was determined using the formation constant of $-\log \beta_{11} = 5.2$ previously reported [1]. The concentration of the 640 nm species was determined as the difference between the total concentration of the plutonyl species and the sum of the aquo and 1:1 species.

The identity of the 640 nm specie was established by accounting for the fate of the H^+ ion added to the equilibrated system. The added hydrogen ion reacted with the polynuclear species to reform the aquo ion, the 1:1 complex and react with the OH^- bound by the polynuclear specie. The final accounting for the OH^- initially bound by the polynuclear specie was therefore the sum of 1) the amount of OH^- needed to raise the pH from that predicted by the amount of acid added and that observed, 2) that associated with the 1:1 complex and 3) that associated with the remaining polynuclear species. The results of this analysis are shown in Table I for an assumed identification of the 640 nm band as the 2:2 and 3:5 hydrolysis product.

Based on the data summarized in Table I, it appears that the 640 nm species is best identified as a species with a 3:5 PuO_2/OH ratio. The potential and observed " OH^- " buffering capacity of this species was 0.0165M and 0.0162M whereas that obtained for the 2:2 complex was 0.0099M and 0.0148M. This observation is consistent with existing predictions and the very strong dependence of the formation of this species on pH that we observed (it would have a $[H^+]^5$ dependence). There is however good reason to question identifying the 640 nm species as a simple hydrolysis product because of the very slow kinetics associated with its reverse hydrolysis reaction. We are therefore investigating the possibility that longer chain polymeric species, with the same PuO_2/OH ratio, may also be present in solution.

Optical Absorption Spectra of Pu(VI) Between pH = 6 to pH = 8

The optical absorption of Pu(VI) in 0.1M sodium perchlorate is shown in Figure 3 at pH = 6.3, 7.4, and 8.1. It is important to note that these solutions were not stable (relative to precipitation) in this pH region. Two hydrolytic species, based on the spectroscopy, were evident. At pH = 6.3 the dominant species is clearly the polynuclear 640 nm species just discussed. A red-shifted shoulder begins to appear at higher pH which corresponds to an absorption with a peak maximum at 655 nm as evident in the pH = 10.5 spectra reported by Kraus and Dam [13].

Whereas the polynuclear species (640 nm band) was stable over a wide pH range, the high-pH hydrolysis product was very unstable at the Pu(VI) concentrations that the optical spectra were recorded (0.012M). The appearance of the 655 nm band was accompanied by precipitation of a plutonium phase. This was especially evident when the pH was adjusted from pH = 7.4 to 8.1. The intensity of the 655 nm shoulder was more strongly dependent on the time elapsed since pH adjustment rather than the pH of the

system. The longer wavelength absorbance appeared to correspond to a steady-state concentration where its formation from the polynuclear species was balanced by its precipitation. This can be seen by comparing the spectra obtained at pH = 7.4 and pH = 8.1. The 655 nm shoulder is stronger in the lower pH spectrum. The major difference between these two, other than pH, was that there was a delay of approximately 2 h prior to taking the pH = 8.1 spectrum.

A clear assignment of the identity of the 655 nm species cannot be established based only on the spectroscopic results presented herein. There are, however, three observations that support identification of this absorption as due to the 1:2 complex: $\text{PuO}_2(\text{OH})_2$. First, the 1:2 complex represents a greater degree of hydrolysis relative to the 3:5 complex which is consistent with its appearance at higher pH. Second, it corresponds to the expected composition of the solid predicted to exist at this pH. This is consistent with the observed precipitation associated with its formation. Third, it was rapidly dissociated when system pH was lowered. Its behavior was therefore more analogous to the monomeric species and it did not exhibit the slow hydrolysis kinetics associated with the 640 nm polynuclear species.

Temperature-Dependent LPAS Spectra of Pu(VI) at pH = 5.3

Preliminary data on the effect of temperature on the equilibration between the 1:1 complex and the aquo species was obtained using LPAS. LPAS spectra at 20°C, 36°C, and 45°C are shown in Figure 4. These were obtained at a total plutonium concentration of $2.6 \times 10^{-4}\text{M}$ and a room-temperature pH of 5.3. Full deconvolution of these spectra has not been completed. There is however very little change observed in the relative concentration of the two species present at room temperature. Continued evaluation of the temperature dependence of the formation constant for the 1:1 complex is in progress.

Comparison of Pu(VI) Speciation Observed with the Predictions of EQ3NR

The speciation of Pu(VI) as a function of pH was calculated using the EQ3NR geochemical code. These results, along with those obtained spectroscopically, are summarized in Table II. Calculations were performed with code version #3245R104 and data library #3245R128. Most calculations were performed for a Pu(VI) concentration of 50 mg/L ($1.8 \times 10^{-4}\text{M}$) in a 0.1N sodium perchlorate medium. Charge balance was performed with the perchlorate ion. It was necessary to set a high Eh (Eh = 1.5 was used) to suppress reduction of the Pu(VI) by the code.

The predictions of the EQ3NR code were compared to the spectra obtained under the same conditions as were input into the code. There were two observations made based on this comparison. The first of these was that the extent of hydrolysis is being underpredicted by the model. This can be seen by comparing the speciation evident in Figure 1 with that predicted at pH = 5.6 in Table II. The dominant species observed in the LPAS spectrum at this pH was the 640 nm band (it is the only species evident at $[\text{Pu}] = 0.0126\text{M}$). The estimated speciation based on the spectrum was: aquo = 24±8%, 1:1 complex = 26±8% with the rest as the 3:5 complex. The prediction of EQ3NR was 66.5%, 29.2%, and 0% respectively with 4% appearing as the 2:2 complex.

A second aspect of this comparison is that the extent that the polynuclear species formed is being underpredicted. At pH = 6, the only species apparent via spectroscopy is the 640 nm species (3:5 complex). This is predicted to comprise only 8% of the hydrolysis products by the EQ3NR code.

The second comparison between the spectra obtained and the predictions of the code is the absence of the 1:2 plutonyl complex $[\text{PuO}_2(\text{OH})_2]$. The existence of this species (1) becomes evident at pH = 6 (see Figure 2); (2) persists, with the exceptions noted, up to pH 8; and (3) is the dominant species reported at pH = 10.5 [13]. The existence of this species is not predicted by EQ3NR and needs to be added to the data base to accurately predict Pu(VI) speciation under repository-relevant conditions.

The effect of temperature on the relative concentration of the aquo Pu(VI) ion and the first hydrolysis product (PuO_2OH^+) was also modeled using EQ3NR. The results of these calculations are shown in Table III. The calculations were done by first equilibrating the Pu(VI) perchlorate systems at a fixed pH. The distribution calculated for perchlorate ion and sodium under the constant pH constraint were then re-entered as the initial concentration of each species. This was then rerun at the same initial temperature with a "floating" hydrogen ion concentration (charge was balanced on $[\text{H}^+]$). The result of this was that observed changes in pH were primarily due to temperature-dependent changes in the speciation rather than charge imbalance present in the initial input parameters.

The qualitative effect of increased temperature was a decrease in pH but a small increase in the relative concentration of the first hydrolysis product. The predictions made by the code were qualitatively confirmed by the spectra reported in Figure 4. This however needs to be further established.

A second aspect of the effect of temperature investigated was also listed in Table II. The qualitative effect of increasing temperature is a decrease in the relative concentration of polynuclear species in favor of the aquo and first hydrolysis product. The temperature dependence of the polynuclear species identified (640 nm band) has not been carefully investigated experimentally due to the complex kinetics associated with the reverse hydrolysis reaction (as reported in a previous section). A decrease in the concentration of the polynuclear species in favor of the formation of the aquo and 1:1 species has however been observed experimentally.

CONCLUSIONS

The major conclusions of this paper were:

1. The 640 nm polynuclear species is best identified as the 3:5 plutonyl hydrolysis product. The possibility that longer-chain polymeric species co-exist with the simpler polynuclear specie cannot be discounted.
2. Two species were observed in the pH range of 6-8 and are expected to persist to pH = 10.
3. It was proposed that the higher-pH species, with an absorption maximum at 655 nm, was the 1:2 uncharged plutonyl complex. This is consistent with our observations but stronger evidence for this assignment needs to be obtained.
4. Comparisons of the observed speciation and those predicted by EQ3NR were made. There was qualitative agreement on the effect of temperature but the current data in the code (1) underpredicts the extent of hydrolysis and (2) does not include data on a species identified in the spectra (presumably the 1:2 complex).

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TABLE I
Calculated and Observed "OH" Capacity of the
640 nm Species for the 2:2 and 3:5 Complex

Identity of 640 nm Species Assumed	Calculated Capacity (M)	Observed "OH" Capacity			Total
		ΔH^+ (M)	[1:1 Complex] (M)	[640 nm Species] (M)	
2:2 Complex	0.0099	0.0107	0.002	0.0021	0.0148
3:5 Complex	0.0165	0.0107	0.002	0.0035	0.0162

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TABLE II
Predicted Speciation of Pu(VI) as a Function
of pH and Total [Pu] Using EQ3NR

pH	PuO ₂ ²⁺ , %	PuO ₂ OH ⁺ , %	2:2, %	3:5, %	Pu, mg/L
pH	98.91	1.09			50
4.5	96.58	3.36			50
5.1	87.23	12.09			50
5.6	66.52	29.17	3.92		50
6.0	39.54	43.57	8.74	8.15	50
7.0	1.8	19.81	1.81	76.59	50
8.0	0.042	4.59	0.084	95.27	50
10.0	0	trace	trace	99.78	50
6.0	22.67	24.93	14.32	38.09	250
6.0	15.92	17.48	14.10	52.49	500
6.0	10.78	11.81	12.88	64.53	1000

TABLE III
Predicted Speciation of Pu(VI) at an Initial
pH of 5.1 and 6.0, Using EQ3NR

Temperature, °C	Aquo, %	1:1, %	2:2, %	3:5, %	pH
21	89.75	9.73	<1	<1	5.1*
21	89.96	9.54	<1	<1	5.09
30	87.86	11.64	<1	<1	4.95
45	83.35	16.14	<1	<1	4.75
60	77.62	21.87	<1	<1	4.58
75	70.89	28.62	<1	<1	4.45
90	63.61	35.95	<1	<1	4.34
21	45.92	39.56	8.57	5.96	6.00*
21	44.90	39.89	8.71	6.50	6.01
45	40.70	51.99	5.35	1.96	5.57
90	32.46	65.96	1.47	0.011	4.89

*pH was held constant for this run.

Figure 1. LPAS Spectrum of $2.6 \times 10^{-4} \text{ M PuO}_2^{2+}$ at pH = 5.6 in 0.1N Sodium Perchlorate

Figure 2. Time-Dependent Spectrum of $0.0099\text{M PuO}_2^{2+}$ (a) at pH = 5.6, time = 0; (b) at pH = 4.7, time = 94 h; and (c) Equilibrated at pH = 4.7

Figure 3. Optical Spectrometry Spectra of $\sim 0.012\text{M}$ PuO_2^{2+} at (a) pH = 6.3, (b) pH = 7.4, and (c) pH = 8.1.

Figure 4. Temperature Dependence of the LPAS Spectrum of PuO_2^{2+} at $\text{pH} = 5.3$ at (a) 20°C , (b) 36°C , and (c) 45°C