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### PLUTONIUM MOBILIZATION AND MATRIX DISSOLUTION DURING EXPERIMENTAL SLUDGE WASHING OF BISMUTH PHOSPHATE, REDOX, AND PUREX WASTE SIMULANTS

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## **PLUTONIUM MOBILIZATION AND MATRIX DISSOLUTION DURING EXPERIMENTAL SLUDGE WASHING OF BISMUTH PHOSPHATE, REDOX, AND PUREX WASTE SIMULANTS**

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### **ABSTRACT**

Consecutive washing of simulant sludges from the BiPO<sub>4</sub> (Cycle 3), Redox, and PUREX processes shows less than 4.5% of sorbed Pu(III/IV) or Pu(VI) is mobilized during CrO<sub>4</sub><sup>2-</sup> dissolution by the 0.01 M NaOH + 0.01 M NaNO<sub>2</sub> sluice or 3.0 M NaOH leach solutions to be used for sludge pretreatment at Hanford. Experimental sludge washing with 2.0 M HNO<sub>3</sub> results in 5.8–65.5% dissolution of Pu(III/IV) or Pu(VI) from all simulants and dissolution of Nd(III), Cr(III), and Fe(III) (where present) from BiPO<sub>4</sub> simulants. The dissolution of Pu(III/IV) and Pu(VI) from BiPO<sub>4</sub> sludge simulants by strongly chelating media is accompanied by dissolution and reduction of Mn(IV) to a Mn(III) complex. Details of radioanalytical and spectroscopic investigations of sludge simulant washing are discussed in the context of understanding actinide behavior during alkaline leaching of radioactive sludge wastes.

## INTRODUCTION

Once the potential of nuclear energy was first realized in 1942, methods for the large-scale production and purification of Pu for defense purposes were rapidly developed. When production of  $^{239}\text{Pu}$  commenced at the Hanford site in 1944, Pu(IV) was coprecipitated with  $\text{BiPO}_4$  while U(VI) remained in solution as a  $\text{SO}_4^{2-}$  complex (1, 2). Plutonium(IV) in the precipitate was oxidized to soluble Pu(VI) by  $\text{BiO}_3^-$ ,  $\text{MnO}_4^-$ , or  $\text{Cr}_2\text{O}_7^{2-}$  prior to secondary coprecipitation with  $\text{LaF}_3$  and final precipitation of Pu(IV) peroxide (1). Bismuth phosphate processing was replaced in 1952 by the Redox solvent extraction process in which Pu(VI) and U(VI) were extracted into methyl isobutyl ketone from concentrated  $\text{Al}(\text{NO}_3)_3$  solutions (3). Separation of Pu(VI) from U(VI) was accomplished by addition of Fe(II), which reduces Pu to the poorly extracted trivalent state.

Tri-*n*-butylphosphate (TBP) was recognized in 1949 as an efficient extractant for the tetra- and hexavalent actinides (3, 4), after which the PUREX process was fully implemented at the Savannah River site by 1954 and later at the Hanford facility (5, 6). PUREX solvent extraction involves the partitioning of U(VI) and Pu(IV) from 3–4 M  $\text{HNO}_3$  into 30% (v/v) TBP in an aliphatic hydrocarbon diluent (e.g., odorless kerosene, normal or branched dodecanes). Recovery of Pu again involves reduction to the trivalent state, principally by U(IV) or Fe(II) (3–6).

Each of these Pu purification methods generated significant volumes of ancillary wastes that have been stored in mild steel single shell (SST) or double shell (DST) tanks. To minimize corrosion of the tank walls by the acidic process wastes, NaOH was used to make the effluent alkaline prior to tank storage (7–9). This pH adjustment, coupled with  $\text{H}_2\text{O}$  evaporation campaigns, has resulted in the formation of precipitates and hydrolytic polymers that have become rather intractable during 50 years of storage at temperatures ranging from ambient external winter conditions to over 93 °C (10) in the presence of an intense radiation field ( $\approx 1 \text{ Ci/L}$  for Hanford wastes (8)).

An understanding of the unique chemical details of each Pu purification process and the subsequent waste management practices is important because state and federal regulations now dictate that these radioactive wastes be remediated. The bulk nonradioactive components of dried sludge materials arising from the  $\text{BiPO}_4$  (Cycle 3), Redox, and PUREX processes are given in Table 1. The principal differences in the waste sludge analyses stem from the unique aspects of the separations process; that is,  $\text{BiPO}_4$  wastes are rich in Bi, La, Mn, and Cr; Redox wastes are largely Al with lesser amounts of Fe and Cr; and PUREX sludges contain mostly Fe with some Al and Mn.

The current sludge pretreatment flowsheet under development at Hanford is presented in Fig. 1. Transfer of solids will be accomplished by sluicing with 0.01 M NaOH + 0.01 M  $\text{NaNO}_2$ , after which the sludge will be leached with 3 M NaOH at elevated temperatures (11, 12). The main objective of this leaching pro-



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**Table 1.** Analyses of Nonradioactive Constituents in Radioactive Waste Sludges and Simulant Sludge Materials

BiPO <sub>4</sub>		BiPO <sub>4</sub> <sup>a</sup> Simulant Analysis <sup>c</sup> %	BiPO <sub>4</sub> (Modified) <sup>a</sup> Simulant Analysis <sup>c</sup> %
Component	Waste Analysis <sup>b</sup> %		
Al + Fe	1.4	0.0	3.9
Bi	23.6	5.5	22.2
Cr	5.3	7.6	6.7
La	10.5	16.9 (La + Nd + Eu)	7.5 (La + Nd + Eu)
Mn	7.2	33.1	24.3
Na	11.8	1.6	3.3
Ti	1.7	0.0	2.6
Anions	12.0	13.8 (P)	8.9 (P)
Volatiles	14.3	NM <sup>d</sup>	NM
O <sub>2</sub>	12.2	21.5	20.6

Redox		PUREX		
Component	Waste Analysis <sup>b</sup> %	Component	Waste Analysis <sup>b</sup> %	Simulant Analysis <sup>c</sup> %
Al	25.4	Al	7.4	NM
Ca	1.5	Ca	1.6	0.7
Cr	3.8	Fe	23.6	29.9
Fe	5.1	K	0.0	0.2
Mn	1.1	Mn	2.2	11.6
Na	15.8	Na	12.2	28.2
Si + Ti	6.2	Si + Ti + Zr	4.9	0.4
Anions	0.5	Anions	1.7	NM
Volatiles	21.0	Volatiles	25.3	NM
O <sub>2</sub>	19.6	O <sub>2</sub>	21.1	28.8

<sup>a</sup> Modifications to the published synthesis are described in the Experimental section. The BiPO<sub>4</sub> (Modified) simulant also contains Al, Ti, and Fe.

<sup>b</sup> Values are in % (w/w) for sludges dried to 120 °C. "Volatiles" represents organics and water lost by firing to 750 °C. O<sub>2</sub> calculated by difference (20).

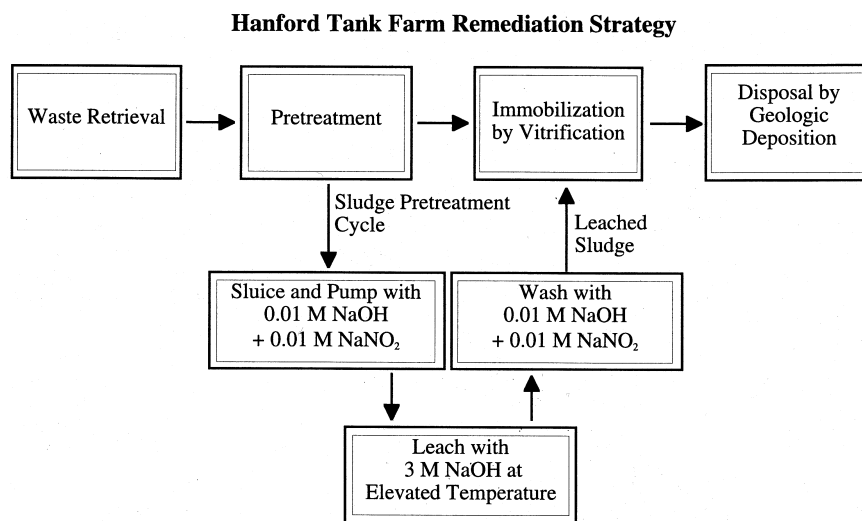
<sup>c</sup> Elemental analyses by EDS (21).

<sup>d</sup> NM = not measured.

cess is to remove P, Al, and Cr, which are incompatible with the current borosilicate glass formulation and which add to the total volume of waste to be vitrified and stored in a deep geologic repository.

For most wastes in the U. S. inventory, the actinide and fission product radioactivities (except the alkaline-soluble <sup>99</sup>TcO<sub>4</sub><sup>-</sup> and <sup>137</sup>Cs<sup>+</sup>) reside in the sludge phase. For example, the sludge material in the SST wastes at Hanford contains >





**Figure 1.** Simplified flowsheet showing the Hanford baseline pretreatment strategy for radioactive sludge materials.

99% of the  $^{90}\text{Sr}$ , U, Pu, and other transuranium elements (9). Partly as a result of these observations, it is believed that the actinides will remain with the sludge during alkaline sluicing and leaching operations. However, this assumption is based on comparatively few direct experimental observations and should be applied only with great caution to such a diverse collection of wastes. Significant chemical variations between tanks have been acknowledged (7-10, 13), and different behaviors can be predicted for SST wastes and DST Complexant Concentrate wastes. For example, high concentrations of complexing agents in the latter may result in greater concentrations of actinide ions in the supernatant. During sludge pretreatment, even minor unexpected mobilization of actinide or fission product radioactivities will cause a major disruption.

The diverse redox chemistry of U, Np, Pu, and, to a lesser extent, Am continues to be widely exploited in actinide separations (1, 2, 14, 15) but may be overlooked in waste remediation, as the latter is focused not on the production of a high quality product but on the quick and economic resolution of a problem (8). Such an approach often relies on broad assumptions (e.g., that the actinides will remain in the sludge phase during washing and leaching operations) and may lead to unexpected results. The complexity of Pu redox chemistry in aqueous media has been discussed (1, 2, 14-16), and significant changes in reduction potentials arise as the pH increases and hydrolysis reactions become important (16-18). In addition, the redox speciation of Pu may be perturbed by complexa-



tion, disproportionation, solubility, and redox interchange reactions (15, 16). The Pu in alkaline radioactive wastes is likely distributed amongst the various hydrolytic polymers and precipitates or is present as a surface sorbed hydrolysis product. The mobilization of sorbed Pu during sludge pretreatment should be of greater concern than its removal from the often intractable hydrolytic polymers; however, the presence of various complexing agents, redox active species, and ongoing radiolysis makes it difficult to accurately predict actinide behavior during alkaline sludge pretreatment.

Focusing on the key factors that influence the redox behavior of Pu, a series of alkaline, acidic, and strongly chelating experimental wash solutions were examined for their propensity to mobilize Pu and to dissolve components of the sludge simulant matrix. In some cases, the release of Pu coincides with component-wise dissolution of the sludge matrix, yielding information about the materials with which Pu is associated. This work details the mobilization of Pu(III/IV), Pu(VI), and several redox active transition metals during consecutive washing of sludge simulants from the BiPO<sub>4</sub> (Cycle 3), Redox, and PUREX processes.

## EXPERIMENTAL

### Reagents

All chemicals were of reagent grade quality and were used as received, except the 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) that was purified as reported previously (19). All H<sub>2</sub>O was deionized using a commercial purification system. All evaporations used gentle heat and were performed under a stream of N<sub>2</sub>. Plutonium-238 was obtained from the inventory at Argonne National Laboratory, and the stock solution was twice evaporated to near dryness over  $\approx$  1 h with 500  $\mu$ L of concentrated HClO<sub>4</sub> to yield <sup>238</sup>Pu(VI). Aliquots of 250  $\mu$ L of 6.0 M HNO<sub>3</sub> and 250  $\mu$ L of 4.6 M HI (14) were combined with the <sup>238</sup>Pu(VI) and the resulting solution was intermittently stirred over 1 h. This <sup>238</sup>Pu-containing solution was pipeted away from the solid I<sub>2</sub> and loaded onto a 1 mL bed of slurry packed TEVA Resin<sup>®</sup> that had been preconditioned by eluting 10.0 mL of 3.0 M HNO<sub>3</sub> under gravity flow. The TEVA resin column retained Pu(IV) while <sup>238</sup>Pu(III) and <sup>238</sup>Pu(VI) were eluted with 10.0 mL of 3.0 M HNO<sub>3</sub>. The <sup>238</sup>Pu(IV) was stripped into 10.0 mL of 1.0 M HCl and then evaporated to near dryness over several hours. A 100  $\mu$ L aliquot of 0.50 M HNO<sub>3</sub> was added to the residue and 33  $\mu$ L was removed and diluted to 100  $\mu$ L with 0.50 M HNO<sub>3</sub> for use as the <sup>238</sup>Pu(III/IV) fraction. Another 33  $\mu$ L of <sup>238</sup>Pu(IV) in 0.50 M HNO<sub>3</sub> was oxidized back to <sup>238</sup>Pu(VI) by two contacts with concentrated HClO<sub>4</sub> as described above. The final <sup>238</sup>Pu(VI) activity was dissolved in 100  $\mu$ L of 0.50 M HNO<sub>3</sub>.



### Synthesis

Preparation of the  $\text{BiPO}_4$  (Cycle 3), Redox, and PUREX sludge simulants at 1/10, 1/15, and 1/10 scales, respectively, followed the published procedures (7), except as noted here. In both  $\text{BiPO}_4$  simulant preparations, 100%  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was substituted with 33.3% each of the hydrated nitrate salts of La, Nd, and Eu. Analyses of  $\text{BiPO}_4$  sludge wastes show that Al, Ti, and Fe are present (20), and 16.4 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 2.4 g  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were dissolved before precipitation of a second  $\text{BiPO}_4$  simulant. Addition of 4.5 g  $\text{TiO}_2$  occurred prior to the pH adjustment with 25% (w/w) NaOH. The remaining synthesis followed that described in the literature (7). This  $\text{BiPO}_4$  simulant containing Al, Ti, and Fe is referred to as the  $\text{BiPO}_4$  (Modified) sludge simulant. Preliminary elemental analyses of the  $\text{BiPO}_4$ ,  $\text{BiPO}_4$  (Modified), and PUREX simulants were performed using energy dispersive spectroscopy (EDS) (21). No EDS investigations of the REDOX simulant were performed due to institutional restrictions on the analysis of radioactive (natural U) samples in the scanning electron microscope.

### Procedures

#### Percent Solids

Percent solids for the sludge simulants were determined by filtering a quantity of the supernatant/sludge slurry on a 40-60  $\mu\text{m}$  glass fritted funnel under water saturated air for 5 min at  $\approx 300$  mm Hg vacuum. A portion of this wet air dried sludge (referred to as the wet sludge) was transferred to a tared vial and dried in an oven at 120  $^\circ\text{C}$  until a constant mass was achieved. Each gravimetric analysis was performed in duplicate to yield the following percent solids:  $\text{BiPO}_4$  = 45.8(6)%,  $\text{BiPO}_4$  (Modified) = 39.6(2)%, Redox = 14.1(1)%, and PUREX = 17.0(2)%. All of the wet sludges were stored in tightly capped containers and were not exposed to air for any lengthy period of time to avoid a change in percent solids.

#### Sludge Washing

All distribution measurements were determined radiometrically by batch contact of the wet sludge with the desired solution at 23(2)  $^\circ\text{C}$  with stirring. Plutonium-238 was counted using standard liquid scintillation techniques and all count rates were corrected for background. The reported percentages of Pu in solution are relative to the activity of Pu initially added to the vessel containing the wet sludge simulant. Glass vessels were used wherever possible, as they have



been reported to sorb lower concentrations of tetravalent actinide ions from neutral pH solutions than polyethylene (22), but sorption to  $\text{SiO}_2$  is well-known (15, 16). It is assumed that losses of  $^{238}\text{Pu}$  by sorption to glass and plastic vessels during experimental manipulations is accounted for in the conservative 15% error assigned to all distribution measurements.

Preliminary  $K_d$  measurements of  $^{241}\text{Am(III)}$  from pH = 11.2(5) (NaOH) solution vs. the solid/solution ratio for the  $\text{BiPO}_4$ ,  $\text{BiPO}_4$  (Modified), Redox, and PUREX simulants were essentially constant over the range 0.0009–0.09 g dry sludge simulant/g solution. Distribution constants of  $^{241}\text{Am(III)}$  from pH = 9.5(5) (NaOH) solution vs. contact time showed that the Redox and PUREX simulants reached a steady state within  $\approx 5$  min, whereas the two  $\text{BiPO}_4$  simulants required  $\approx 40$  min. A conservatively long contact time of 180 min was employed for loading  $^{238}\text{Pu}$  onto the sludge simulants.

Plutonium-238 was loaded onto each sludge simulant by adding  $\approx 20 \mu\text{L}$  of  $^{238}\text{Pu(III/IV)}$  or  $^{238}\text{Pu(VI)}$  in 0.50 M  $\text{HNO}_3$  to 8.5 mL of pH = 9.5(5) (NaOH) solution. After mixing, 100  $\mu\text{L}$  aliquots of  $^{238}\text{Pu(III/IV)}$  or  $^{238}\text{Pu(VI)}$  were radiometrically assayed. A 1.0 mL aliquot of the desired  $^{238}\text{Pu(III/IV)}$  or  $^{238}\text{Pu(VI)}$  solution was added to a known mass of wet sludge (average mass = 0.15(4) g) and centrifuged for 1 min. The mixture was stirred gently for 180 min, centrifuged for 2 min, and the supernatant was pipeted away (carefully avoiding removal of solid material) and filtered before radiometric assay. Removal of  $^{238}\text{Pu}$  from these weakly alkaline solutions ranges from 99.8 to 100%. Each sludge simulant loaded with  $^{238}\text{Pu}$  was then contacted with 1.0 mL of a simplified tank waste supernatant simulant containing 0.10 M  $\text{Na}_2\text{CO}_3$  + 0.50 M NaOH + 1.0 M  $\text{NaNO}_3$  for 22 h with gentle stirring. Each sample was centrifuged for 2 min, the supernatant pipeted away, and an unfiltered 100  $\mu\text{L}$  aliquot taken for radiometric assay. The remaining solution was filtered through a 0.45  $\mu\text{m}$  PTFE syringe tip filter to remove suspended solids, and 100  $\mu\text{L}$  was assayed radiometrically to determine the concentration of dissolved  $^{238}\text{Pu}$ . "Dissolved Pu" is operationally defined here as that fraction passing through a 0.45  $\mu\text{m}$  PTFE filter.

The seven consecutive sludge wash solutions (0.01 M NaOH + 0.01 M  $\text{NaNO}_2$ , 3.0 M NaOH,  $\text{H}_2\text{O}$ , 0.05 M glycolic acid + 0.10 M NaOH, 0.10 M  $\text{HNO}_3$ , 2.0 M  $\text{HNO}_3$ , and 0.50 M HEDPA) were contacted with the residual  $^{238}\text{Pu}$ -spiked sludge simulant (i.e., the solid remaining after contact with the simplified tank waste supernatant simulant) in the following manner. One mL of the first wash solution was added to each residual  $^{238}\text{Pu}$ -spiked sludge simulant and stirred for 30 min. After 2 min of centrifugation, the solution was pipeted away and both unfiltered and filtered samples were assayed radiometrically. Residual sludge material was then consecutively contacted with 1.0 mL of the remaining wash solutions according to the procedure described above.

Sludge simulant washing for the visible spectroscopic analyses employed the same procedures described for the seven consecutive wash experiments, ex-





cept that 0.13(1) g of each wet sludge simulant was contacted with 2.0 mL of the respective wash solution. All samples were filtered through a 0.45  $\mu\text{m}$  PTFE filter prior to data collection against the relevant background solution. Absorbance data were collected on a Cary-14 spectrometer with an OLIS upgrade package using 1.0 cm path length disposable methacrylate cuvettes. Standard spectra were collected on  $2 \times 10^{-4}$  M  $\text{Na}_2\text{CrO}_4$  in 3.0 M NaOH, 0.4 M  $\text{Fe}(\text{NO}_3)_3$  in 2.0 M  $\text{HNO}_3$ , 0.01 M  $\text{Mn}(\text{NO}_3)_2$  in 0.50 M HEDPA,  $2 \times 10^{-4}$  M  $\text{KMnO}_4$  in  $\text{H}_2\text{O}$ , and (initially)  $2 \times 10^{-3}$  M  $\text{KMnO}_4$  in 0.45 M HEDPA. Additional solids washing experiments involved parallel contact of 0.12(3) g of the wet  $\text{BiPO}_4$  or  $\text{BiPO}_4$  (Modified) simulants with 2.0 mL of 0.05 M glycolic acid, 0.10 M NaOH, or 0.05 M glycolic acid + 0.10 M NaOH using the procedure described above. Washing of 0.1862 g of a freshly precipitated slurry of green Cr(III) hydrolysis products with 2.0 mL of 2.0 M  $\text{HNO}_3$  and washing of 0.0044 g  $\text{MnO}_2$  with 5.0 mL of 0.50 M HEDPA were also performed using a similar procedure.

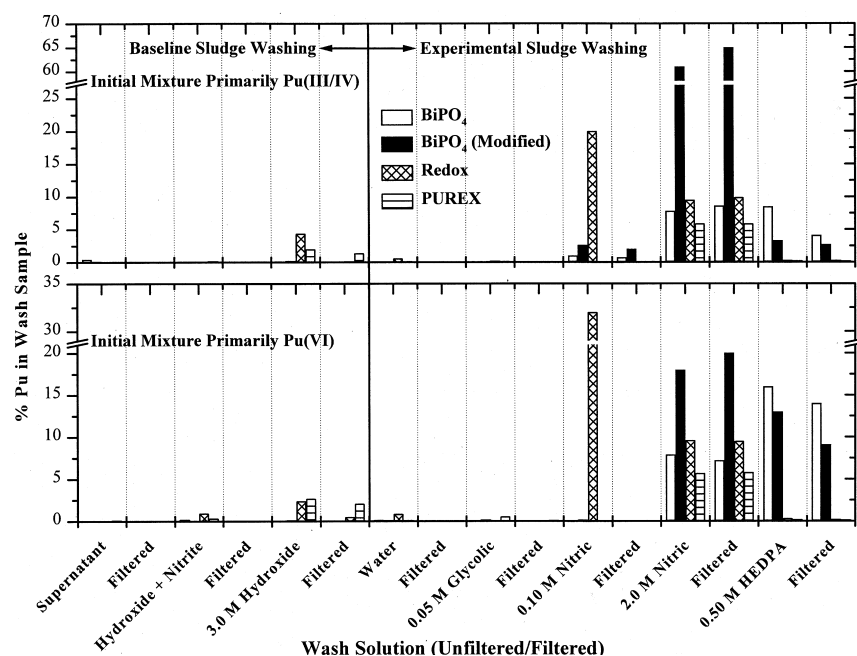
## RESULTS AND DISCUSSION

Minor changes to the published synthesis (7) of the two  $\text{BiPO}_4$  sludge simulants were made to provide multiple spectroscopic probes for the lanthanides and so that the simulant compositions would more closely resemble the actual sludge wastes. As discussed in the Experimental section, 100% La was substituted with 33.3% each of La, Nd, and Eu in both  $\text{BiPO}_4$  simulants. Because Al, Ti, and Fe are present in actual sludge samples (Table 1) and because actinides are known to sorb to oxide surfaces (15, 16, 23), these elements were added to the simulant referred to as  $\text{BiPO}_4$  (Modified).

Due to the heterogeneous nature of the sludge simulants and limitations of the EDS analytical sampling technique, minor differences exist between the compositions reported in Table 1 for the actual waste materials and the simulants prepared here. In general, the EDS results (21) compare favorably with the wet chemical waste analyses (20), except that the  $\text{BiPO}_4$ ,  $\text{BiPO}_4$  (Modified), and PUREX simulants prepared here contain 3-5 times more Mn than found in the actual wastes.

Fig. 2 shows that the mobilization of sorbed Pu(III/IV) or Pu(VI) by the simplified tank waste supernatant solution and the baseline 0.01 M NaOH + 0.01 M  $\text{NaNO}_2$  sluice medium is negligible ( $\leq 1.0\%$ ) for all sludge simulants. Exposure of the Redox and PUREX sludge simulants to 3.0 M NaOH facilitates release of 4.4% and 2.0% Pu(III/IV), respectively, in unfiltered samples. Release of Pu(VI) into 3.0 M NaOH reaches 2.4% for the Redox material and 2.7% for the PUREX simulant. As transport of actinides by suspended solids is well-known (16, 23) and highly probable during sludge pretreatment, filtered samples were also assayed to permit discrimination of dissolved Pu species from Pu associated with suspended





**Figure 2.** % Pu in unfiltered and filtered wash solutions after contact with the  $\text{BiPO}_4$ ,  $\text{BiPO}_4$  (Modified), Redox, or PUREX sludge simulants at 23(2) °C.

solids. After filtration, the percentages of Pu(III/IV) in 3.0 M NaOH decrease to 0.1% and 1.4% for the Redox and PUREX wash solutions, respectively. Plutonium(VI) dissolution (i.e., after filtration) for the same two sludge simulants is 0.5% and 2.1%. The difference between the filtered and unfiltered samples of 3.0 M NaOH is greatest for the Redox simulant and may be related to the leaching of Al by 3.0 M NaOH (11, 12). Conversely, the similarity in the percentages of Pu(III/IV) or Pu(VI) in unfiltered and filtered 3.0 M NaOH PUREX wash solutions suggests the presence of dissolved Pu species.

Release of Pu into H<sub>2</sub>O or 0.05 M glycolic acid + 0.10 M NaOH wash solutions is low ( $\leq 0.9\%$ ) for all simulants. Upon contact of the sludge simulants with 0.10 M HNO<sub>3</sub>, however, mobilization of Pu(III/IV) increases from all but the PUREX simulant. The percentages of Pu(III/IV) removed from  $\text{BiPO}_4$  and  $\text{BiPO}_4$  (Modified) simulants by 0.10 M HNO<sub>3</sub> decrease by  $\approx 25\%$  upon filtration, suggesting that  $\approx 75\%$  of the Pu(III/IV) is a dissolved species. Release of Pu(III/IV) (19.5%) and Pu(VI) (31.6%) from the Redox sludge simulant is noteworthy, as is the yellow color (explained below) of the wash solution. Neither Pu(III/IV) nor Pu(VI) are liberated from the PUREX materials by 0.10 M HNO<sub>3</sub>, although the wash solutions are a deep reddish brown. It should be noted



that the 0.10 M  $\text{HNO}_3$  wash solutions for the Redox and PUREX simulants could not be filtered due to high concentrations of suspended solids that were not settled by centrifugation.

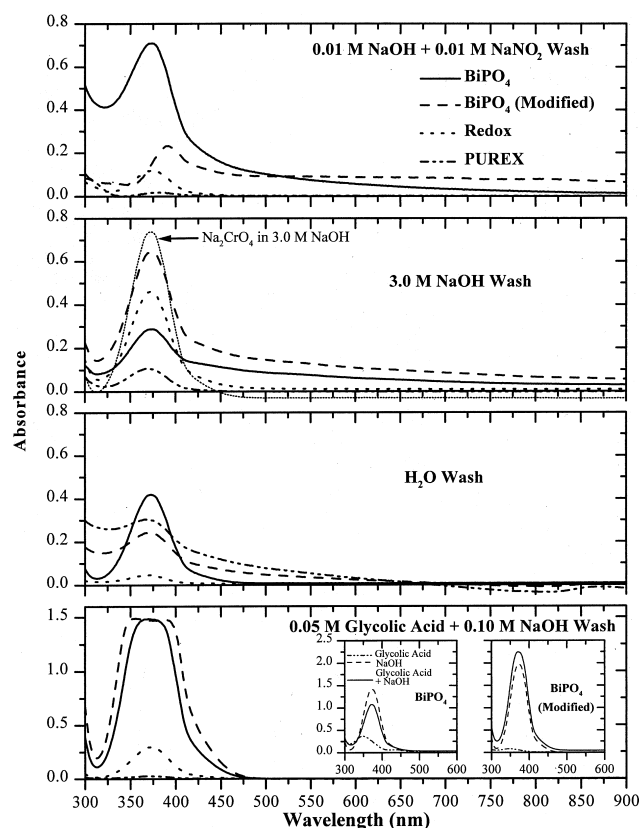
As expected, sludge washing with 2.0 M  $\text{HNO}_3$  effects significantly greater dissolution of Pu (note the close similarities in the % Pu for the filtered and unfiltered samples) from all four sludge simulants. The  $\text{BiPO}_4$  (Modified) sludge yields up to 7.6 times more Pu(III/IV) in solution than does the  $\text{BiPO}_4$  simulant that is void of Al, Ti, and Fe. In fact, the highest Pu dissolution (Pu(III/IV) = 65.5% and Pu(VI) = 19.7%) is observed from the  $\text{BiPO}_4$  (Modified) simulant. Mobilization of dissolved Pu from the Redox sludge simulant is far less than from 0.10 M  $\text{HNO}_3$ , but still significant at 9.5% for Pu(III/IV) and 9.6% for Pu(VI). Plutonium dissolution from PUREX materials by 2.0 M  $\text{HNO}_3$  reaches 5.9% and 5.8% for Pu(III/IV) and Pu(VI), respectively.

The final sludge wash employed the very strong chelating agent HEDPA (19, 24, 25). Contact with 0.50 M HEDPA does not effect Pu removal greater than 0.4% from either the Redox or PUREX sludges; however, removal of Pu(III/IV) (maximum = 8.5%), and especially Pu(VI) (maximum = 15.9%), from the  $\text{BiPO}_4$  simulants is observed.

Cumulative dissolution of Pu(III/IV) during the seven consecutive sludge simulant wash procedures is 13.5%, 70.2%, 10.5%, and 7.5% for filtered wash solutions from the  $\text{BiPO}_4$ ,  $\text{BiPO}_4$  (Modified), Redox, and PUREX materials, respectively. Cumulative dissolution of Pu(VI) is greatest for the  $\text{BiPO}_4$  simulants:  $\text{BiPO}_4$  = 21.6%,  $\text{BiPO}_4$  (Modified) = 28.8%, Redox = 10.4%, and PUREX = 8.3%. The most significant difference lies in the overall removal of 70.2% Pu(III/IV) and 28.8% Pu(VI) from the  $\text{BiPO}_4$  (Modified) simulant. This observation is not in agreement with the well-known selectivity of  $\text{BiPO}_4$  to coprecipitate Pu(III/IV) over the plutonyl ions and cannot be explained at present.

During the course of sludge washing, yellow, blue, reddish brown, and purple colors were observed for different wash solutions from different sludge simulants. Such an observation is not unexpected given the presence of various transition metals in the sludge simulants and the likelihood of their dissolution by the more chemically aggressive wash solutions. Visible spectroscopy was used to help identify which transition metals are mobilized during sludge washing. Fig. 3 shows four sets of absorption spectra for contact of  $\text{BiPO}_4$ ,  $\text{BiPO}_4$  (Modified), Redox, or PUREX sludge simulants with 0.01 M NaOH + 0.01 M  $\text{NaNO}_2$ , 3.0 M NaOH,  $\text{H}_2\text{O}$ , and 0.05 M glycolic acid + 0.10 M NaOH. An objective of the Hanford baseline sludge pretreatment operation is removal of Cr from the solids targeted for vitrification (11, 12), and related experiments have established  $\lambda_{\text{max}}$  for  $\text{CrO}_4^{2-}$  of 373 nm in 0.2-3 M NaOH (26). Broad, nondescript peaks are observed for 0.01 M NaOH + 0.01 M  $\text{NaNO}_2$  wash solutions of the  $\text{BiPO}_4$  (Modified), Redox, and PUREX simulants. The spectrum observed for the  $\text{BiPO}_4$  simulant can be attributed to dissolution of  $\text{CrO}_4^{2-}$ .





**Figure 3.** Absorption spectra of wash solutions after contact with  $\text{BiPO}_4$ ,  $\text{BiPO}_4$  (Modified), Redox, or PUREX sludge simulants. The small inset spectra for 0.05 M glycolic acid + 0.10 M NaOH show that glycolic acid alone does not effectively dissolve  $\text{CrO}_4^{2-}$ .

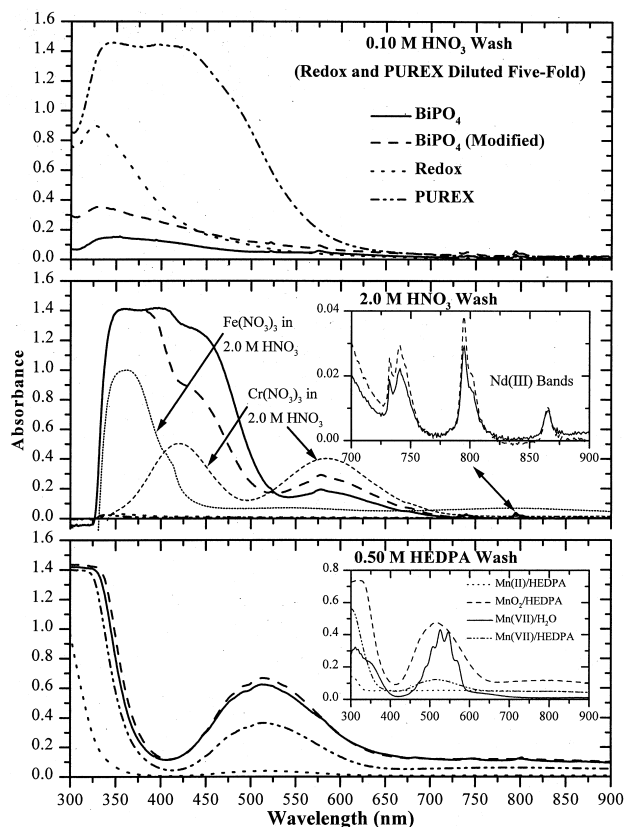
Contact of the  $\text{BiPO}_4$ ,  $\text{BiPO}_4$  (Modified), and Redox simulants with 3.0 M NaOH afford spectra that compare favorably with the  $\text{Na}_2\text{CrO}_4$  standard spectrum. The comparatively low absorbance for the  $\text{BiPO}_4$  simulant may be an artifact of Cr depletion by the preceding wash. In general, the  $\text{BiPO}_4$  sludge simulants release more  $\text{CrO}_4^{2-}$  than the Redox simulant, which is consistent with the higher Cr concentration of the  $\text{BiPO}_4$  sludge simulants.

Interstitial liquids remaining in the solids upon the crossover from 3.0 M NaOH to  $\text{H}_2\text{O}$  likely contribute to the broad bands below 425 nm observed in the  $\text{H}_2\text{O}$  wash solution, and few conclusions can be drawn from these spectra. Addition of 0.05 M glycolic acid + 0.10 M NaOH to the  $\text{BiPO}_4$  and  $\text{BiPO}_4$  (Modified) sludge simulants results in greater  $\text{CrO}_4^{2-}$  dissolution than observed previously.



Because the solids have already been contacted with 3.0 M NaOH, enhanced dissolution of Cr by glycolic acid may be postulated. As the inset spectra for the  $\text{BiPO}_4$  and  $\text{BiPO}_4$  (Modified) simulants show, however, Cr removal by 0.05 M glycolic acid + 0.10 M NaOH is comparable to that achieved by contact with 0.10 M NaOH alone. The apparent increase in  $\text{CrO}_4^{2-}$  dissolution from the two  $\text{BiPO}_4$  simulants may be related to slow dissolution kinetics (12) or to "activation" by the preceding wash solutions (13).

Fig. 4 shows the spectra obtained from sludge washing by 0.10 M  $\text{HNO}_3$ , 2.0 M  $\text{HNO}_3$ , and 0.50 M HEDPA. The top panel of Fig. 4 shows very broad bands that can be attributed to Fe(III) based on the yellow to reddish brown col-



**Figure 4.** Absorption spectra of acidic wash solutions after contact with  $\text{BiPO}_4$ ,  $\text{BiPO}_4$  (Modified), Redox, or PUREX sludge simulants. The small inset spectra for 0.50 M HEDPA shows that washing of  $\text{MnO}_2$  with 0.50 M HEDPA affords a spectrum similar to that observed for the two  $\text{BiPO}_4$  sludge simulants.



ors of the solution, the sludge compositions (Table 1), and by comparison to the  $\text{Fe}(\text{NO}_3)_3$  standard spectrum in 2.0 M  $\text{HNO}_3$  (middle panel). So much Fe was dissolved by 0.10 M  $\text{HNO}_3$  that the Redox and PUREX wash solutions required five-fold dilution to permit filtration and to afford reasonable absorbances. In agreement with the compositions shown in Table 1, the absorbances at 362 nm decrease with the Fe content:  $\text{PUREX} > \text{Redox} > \text{BiPO}_4$  (Modified). The relative ease with which Fe was dissolved by 0.10 M  $\text{HNO}_3$  suggests that it is not present as goethite ( $\alpha\text{-FeOOH}$ ), but possibly as the more easily dissolved  $\text{Fe}(\text{OH})_3$ , ferrihydrite ( $\text{FeOOH}_{\text{am}}$ ), or hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ).

Release of Cr(III) from the  $\text{BiPO}_4$  and  $\text{BiPO}_4$  (Modified) simulants into 2.0 M  $\text{HNO}_3$  is significant, as is dissolution of Fe from the  $\text{BiPO}_4$  (Modified) simulant. The broad spectrum obtained for the  $\text{BiPO}_4$  sludge simulant is likely due to the presence of multiple Cr species, including hydrolysis products, that are not well characterized (27, 28). The spectrum obtained for the 2.0 M  $\text{HNO}_3$  wash of the  $\text{BiPO}_4$  (Modified) simulant is sufficiently detailed, however, to permit a visual deconvolution into spectral contributions from Fe(III) and Cr(III). A closer examination of the 700-900 nm region in both the 0.10 M and 2.0 M (inset)  $\text{HNO}_3$  wash solutions from the  $\text{BiPO}_4$  simulants shows very weak bands at 732, 741, 795, and 865 nm that are characteristic for Nd(III) in 2.0 M  $\text{HNO}_3$  (29). The low absorbances for 2.0 M  $\text{HNO}_3$  wash solutions from the Redox and PUREX sludge simulants indicate that Fe is almost quantitatively removed from these simulants by the preceding 0.10 M  $\text{HNO}_3$  wash.

Contact of the  $\text{BiPO}_4$ ,  $\text{BiPO}_4$  (Modified), and PUREX simulants with 0.50 M HEDPA generates wash solutions purple in color. The visible spectra of these solutions show symmetric, almost featureless broad bands centered at  $\approx 513$  nm, in contrast to the  $\text{MnO}_4^-$  spectrum in  $\text{H}_2\text{O}$  (inset). There is no absorption above 375 nm in the wash solution from the Redox sludge, which contains the least Mn (Table 1). Confirmation that the broad 513 nm band is due to a Mn species was accomplished by washing pristine  $\text{MnO}_2$  with 0.50 M HEDPA, which affords a spectrum that closely matches those from the  $\text{BiPO}_4$ ,  $\text{BiPO}_4$  (Modified), and PUREX simulant washes. Manganese(IV) dioxide is known to undergo complicated redox reactions with various organic and inorganic complexants (30, 31) and additional data were needed to unambiguously identify the oxidation state of Mn. Experiments wherein Mn(II) was combined with 0.45 M HEDPA yielded no interesting spectral features; however, reaction of  $\text{MnO}_4^-$  with 0.50 M HEDPA did result in a weak band centered at 513 nm that resembles the spectrum of the  $\text{MnO}_2$ /HEDPA wash solution.

Examination of standard spectral data (32) for aqueous Mn(III) shows  $\lambda_{\text{max}}$  values of  $\approx 500\text{-}550$  nm (depending on aqueous medium) with a strong high energy band sharply increasing in absorption below 400 nm. Manganese(IV), however, yields  $\lambda_{\text{max}}$  near 650 nm with a sharply increasing absorption band below 550 nm. Based on these standard spectra and related experiments (33), it can be



deduced that a Mn(III)/HEDPA complex is likely responsible for the broad bands observed in the 0.50 M HEDPA wash solutions from the BiPO<sub>4</sub>, BiPO<sub>4</sub> (Modified), and PUREX sludge simulants.

## CONCLUSIONS

Some Pu is liberated with CrO<sub>4</sub><sup>2-</sup> (and AlO<sub>2</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> (11, 12)) during the Hanford baseline sludge pretreatment operations. Up to 4.4% Pu(III/IV) was observed in an unfiltered 3.0 M NaOH wash sample from the Redox sludge simulant. This value decreases to 0.1% after filtration and underscores the possibility of transport by suspended solids. Experimental sludge washing by 0.10 M HNO<sub>3</sub> releases the majority of the Fe from both the Redox and PUREX simulants, with the Redox simulant simultaneously releasing 19.5% Pu(III/IV) and 31.6% Pu(VI). Despite almost quantitative removal of Fe from the PUREX sludge simulant by 0.10 M HNO<sub>3</sub>, no Pu is liberated indicating that the Pu is strongly retained by the residual insoluble sludge fraction. It is worth noting that the 0.10 M HNO<sub>3</sub> wash reduced the overall volume of the residual PUREX simulant by ≈ 75%, which is comparable to that obtained in related studies (13). Sludge washing with 2.0 M HNO<sub>3</sub> results in significant releases of Pu(III/IV), Pu(VI), Cr(III), Ln(III) (Ln = La, Nd, Eu), and Fe(III) (where present) from the BiPO<sub>4</sub> simulants. Dissolution of Pu by 0.50 M HEDPA is probably due to the combined stability of the actinide/HEDPA complexes (19, 24, 25) and the dissolution of MnO<sub>2</sub> to which actinides are known to sorb (15, 16, 23).

It is clear that transport of actinide ions by suspended solids is likely to be an important migratory pathway that will require careful process control during sludge pretreatment operations. The dissolution of redox active transition metals occurs during both Hanford baseline sludge pretreatment and experimental sludge washing, and the influence of redox reactions involving Cr, Fe, or Mn on actinide behavior during alkaline sludge pretreatment operations is not yet well understood. Future efforts will focus on the preparation of sludge simulants in which Pu is present during the precipitation/hydrolysis reactions and on correlating Pu mobilization with transition metal dissolution by the various sludge wash solutions. The effects of radiolytic and thermal "aging" of sludge simulants will also be investigated as will the electrochemical behavior of An(V/VI/VII) (An = Np, Pu) in alkaline media.

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