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### Oxidative Alkaline Leaching of Americium from Simulated High-Level Nuclear Waste Sludges

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## Oxidative Alkaline Leaching of Americium from Simulated High-Level Nuclear Waste Sludges

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**Abstract:** Oxidative alkaline leaching has been proposed to pretreat the high-level nuclear waste sludges to remove some of the problematic (e.g., Cr) and/or nonradioactive (e.g., Na, Al) constituents before vitrification. It is critical to understand the behavior of actinides, americium and plutonium in particular, in oxidative alkaline leaching. We have studied the leaching behavior of americium from four different sludge simulants (BiPO<sub>4</sub>, BiPO<sub>4</sub> modified, Redox, PUREX) using potassium permanganate and potassium persulfate in alkaline solutions. Up to 60% of americium sorbed onto the simulants is leached from the sludges by alkaline persulfate and permanganate. The percentage of americium leached increases with [NaOH] (between 1.0 and 5.0 M). The initial rate of americium leaching by potassium persulfate increases in the order BiPO<sub>4</sub> sludge < Redox sludge < PUREX sludge. The data are most consistent with

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oxidation of  $\text{Am}^{3+}$  in the sludge to either  $\text{AmO}_2^+$  or  $\text{AmO}_2^{2+}$  in solution. Though neither of these species is expected to exhibit long-term stability in solution, the potential for mobilization of americium from sludge samples would have to be accommodated in the design of any oxidative leaching process for real sludge samples.

**Keywords:** Americium, High-level nuclear waste, Oxidative leaching

## INTRODUCTION

Large quantities of nuclear wastes are stored in underground tanks across the U.S. Department of Energy complex. At the Hanford site in Washington, a total of 177 underground tanks contain  $1.4 \times 10^5 \text{ m}^3$  of wastes with  $1.7 \times 10^8$  curies of radioactivity (1). These wastes were generated during a period of more than 40 years of industrial-scale reprocessing of spent nuclear fuel to produce plutonium (1). The acidic effluents of the reprocessing schemes were made alkaline to reduce corrosion of the mild steel linings of the tanks and to precipitate metal hydroxides. After a few decades of storage, the nuclear wastes in the Hanford tanks have stratified into three layers: supernatant liquid, salt cake (primarily water-soluble sodium salts), and solid sludge. The densest layer is the solid sludge, which is made up of metal oxides and hydroxides. The sludge contains the majority of the actinide elements and other radionuclides and so represents most of the high-level waste (HLW) in the tanks. The current strategy for the management of these wastes calls for the vitrification of HLW sludge prior to disposal in a mined geologic repository (2).

Besides the radioactive materials, the sludge also contains large amounts of nonradioactive components such as sodium and aluminum, and significant amounts of “problematic” elements such as chromium. The presence of sodium and aluminum increases the volume of HLW and thus the volume of vitrified glass, while the presence of chromium complicates the vitrification operation and adversely affects the quality of the glass product because it forms spinel-type crystalline phases in the glass melter (3). Since the vitrification process is very costly (it is estimated that a canister of vitrified high-level waste costs \$1 million), pretreatment of the sludge is desirable to remove as many of the nonradioactive and/or problematic constituents as is practical, thus significantly reducing the volume of glass to be produced.

Though alkaline scrubbing has proven reasonably effective for removing aluminum by converting aluminum oxides/hydroxides into soluble aluminates (4), this treatment is less effective for the removal of chromium. As an alternative, leaching the sludge with alkaline solutions containing oxidants (“oxidative alkaline leaching”) has been proposed and tested. A previous study has shown that ferrate and permanganate effectively remove chromium from the sludge by oxidizing insoluble Cr(III) to soluble Cr(VI) (5).

Before the oxidative alkaline leaching can be reliably utilized in sludge pretreatment, the effect of oxidants on the radionuclides in the sludge, actinides in particular, must be investigated. Treating the sludge with oxidative alkaline leachates could generate conditions under which the oxidation states of actinides change and normally insoluble actinide compounds [e.g., the hydroxides of Am(III), Pu(IV) and Np(IV)] can no longer be reliably assumed to remain in the sludge phase. In fact, it has been reported that the concentration of plutonium in the leachate was increased in oxidative leaching (6). A preliminary study from this group also shows that the presence of  $K_2S_2O_8$  could increase the concentration of americium in the leachate by 10–20% at 85°C (7). Clearly this is an adverse outcome, as the purpose of sludge washing is to remove the non-radioactive and/or problematic constituents while concentrating the actinides in the sludge. These preliminary and limited data (6, 7) indicate that a comprehensive understanding of the chemical behavior of actinides (americium and plutonium in particular) in oxidative alkaline leaching is critical to the development of the strategies for HLW sludge pretreatment.

The HLW sludges at Hanford contain a variety of wastes from different reprocessing schemes including the  $BiPO_4$  coprecipitation process, and the Redox and PUREX solvent extraction processes. The radionuclides in the sludge in a given tank could well exist in different chemical environments and thus demonstrate different chemical behaviors during sludge washing. For example, a previous study on the leaching of uranium (7) suggests that uranium may be associated with phosphate in the  $BiPO_4$  sludge, but exists as hydrous oxides in the Redox sludge. To evaluate the effect of sludge matrix, it is necessary to study oxidative alkaline leaching with well-characterized sludges. In the present work, we have chosen to use the simulated sludges prepared according to the historical processes including  $BiPO_4$ , Redox, and PUREX (2). Oxidative alkaline leaching of americium with  $K_2S_2O_8/NaOH$  and  $KMnO_4/NaOH$  is studied under varying concentrations of the oxidant and alkalinity, and at different temperatures.

## EXPERIMENTAL

### Chemicals and Equipment

Deionized water from a MilliQ system was used to prepare all solutions.  $NaOH$ ,  $HNO_3$ ,  $HCl$ ,  $KMnO_4$ , and  $K_2S_2O_8$  were of reagent grade and used as received.  $^{243}Am$  was obtained from the inventory at Lawrence Berkeley National Laboratory and purified by cation exchange. The  $\alpha$ -spectrum of the purified  $^{243}Am$  solution showed two peaks at 5.28 MeV ( $\sim 88\%$ ) and 5.23 MeV ( $\sim 11\%$ ), confirming the purity of the  $^{243}Am$  stock solution (in 0.5 M  $HNO_3$ ). The  $\alpha$ -activity was measured on a Perkin Elmer Liquid

Scintillation counter (model number 1414), using Ecolume (ICN Biomedicals) as the scintillation solution.

### Sludge Preparation and Leaching

Four simulated sludges ( $\text{BiPO}_4$ ,  $\text{BiPO}_{4\text{modified}}$ , Redox, and PUREX sludges) were prepared at Argonne National Laboratory based on the formulae reported by Kupfer (2). The  $\text{BiPO}_{4\text{modified}}$  sludge was prepared with a slightly modified formulae of the  $\text{BiPO}_4$  sludge in which the lanthanum was partially substituted with neodymium and europium (as spectroscopic probes) and small amounts of titanium, aluminum, and iron were introduced to simulate actual sludge samples. Because the  $\text{BiPO}_4$  process relied on co-precipitation of actinides in  $\text{BiPO}_4$  and  $\text{LaF}_3$  solid phases, these sludges are dominated by  $\text{BiPO}_4$  and  $\text{LaF}_3$ . Our prior analysis indicates that the  $\text{BiPO}_4$  and  $\text{BiPO}_{4\text{modified}}$  simulants also contain 5.3–7.6% by weight chromium, 7.2% manganese, and minimal iron. The Redox sludge simulant, derived from the effluents of solvent extraction from concentrated  $\text{Al}(\text{NO}_3)_3$  solutions, is dominated by  $\text{Al}_2\text{O}_3$ , but also contains 3.8% chromium, 5.1% iron, and 1.1% manganese. The PUREX sludge simulant is primarily oxides of iron with lesser amounts of  $\text{Al}_2\text{O}_3$ , minimal chromium plus 2.2% manganese. Each simulant also contains 12–16% sodium. Detailed information on the composition and characterization of the sludge simulants has been provided in an earlier report (8). We are aware that the particle size could have significant effect in leaching experiments (9, 10). Therefore, the sludges in this study were prepared in powder form and pulverized to pass through a 20-mesh screen to reduce the size effect.

### Leaching Method

The oxidative leaching experiments were conducted in two steps: 1) sorption of Am(III) onto the sludge from a solution designed to simulate the waste tank supernatant; 2) leaching the americium from the sludge with alkaline solutions in the presence of various oxidants. In the first step, approximately 0.05 g of each of the sludges was contacted with 4 mL of 0.1 M  $\text{Na}_2\text{CO}_3$ /0.5 M  $\text{NaOH}$ /1 M  $\text{NaNO}_3$  solution (which is representative of the supernatant solution in the Hanford tanks) containing 0.1 to 0.4  $\mu\text{Ci}$   $^{243}\text{Am}$  in 15 mL polyethylene centrifuge tubes. The plastic tubes were used instead of glass vessels because a previous study had shown that americium was sorbed onto the surface of borosilicate glass under alkaline conditions (11). The tubes were shaken for a period of at least 24 h to allow sufficient time for the americium to be sorbed onto the sludge. The samples were centrifuged and the  $\alpha$ -activity of the supernatant was determined by liquid scintillation

counting. It was found that 95% of the americium was sorbed onto the Redox and PUREX sludges ( $K_d \approx 1500 \text{ mL/g}$ ), and 99% onto the  $\text{BiPO}_4$  sludges ( $K_d \approx 8000 \text{ mL/g}$ ). The supernatant was then discarded, and the sludges loaded with americium were retained in the centrifuge tubes. The americium on the sludge could be either sorbed or coprecipitated, which cannot be distinguished in our experiments. However, we consider the surface-sorbed americium representative of a substantial fraction of the americium likely present in actual sludge samples. Besides, the subtle distinction between sorption and precipitation may not be important if significant penetration of the sludge matrix by the leachate is achieved during leaching. Sorbed and coprecipitated americium will therefore be equally vulnerable to oxidative leaching in actual sludge samples. In the second step, 4 mL of leaching solution with appropriate concentrations of NaOH and oxidant were added to each tube containing the sludge loaded with americium. The samples were shaken for varying periods of time and centrifuged. Aliquots of the supernatant solution were taken and analyzed by LSC to determine the amount of americium leached from the sludges. Most of the leaching experiments were conducted with 0.1 M solutions of  $\text{K}_2\text{S}_2\text{O}_8$  or  $\text{KMnO}_4$  in 1, 3, or 5 M NaOH. For the leaching of americium from the  $\text{BiPO}_4$  sludge with alkaline  $\text{KMnO}_4$  or  $\text{K}_2\text{S}_2\text{O}_8$  solutions, parallel experiments were conducted at 25 and 70°C to evaluate the effect of temperature. Quantitative dissolution of all americium present in the sludge sample into the 4 mL of leachant would result in a solution of  $1.4 \times 10^{-6} \text{ M}$  in americium.

To assess the potential impact of consecutive leaching on Am mobilization, a second leaching of the sludge samples with alkaline permanganate was performed as follows. The supernatant containing americium leached in the first contact was carefully removed from the tubes leaving the remaining undissolved sludge behind. To the tubes was added 4 mL of fresh solution with 0.1 M  $\text{KMnO}_4$  and appropriate concentration of NaOH. Again these were shaken for a period of time and aliquots of supernatant were taken and analyzed by LSC. Duplicate samples generally agreed within 1–2%. Control samples representing that expected from complete dissolution of the Am into 4 mL of the leachant were also counted. The percentages of americium leached from the sludges were normalized against the counting results of the control samples.

To check the mass balance of americium in the sorption and leaching experiments, the amount of americium sorbed onto the inner wall of the tubes was checked by removing the suspensions from the tubes and washing the tubes with 6 M  $\text{HNO}_3$ . The amount of americium in the nitric acid washing accounted for less than 1–2% of total americium, suggesting the sorption on the wall was insignificant. In a limited number of multiple-step leaching experiments that are discussed in subsequent sections, the recovery of americium is higher than 95%, confirming that the mass balance of americium in the experiments was satisfactory.

## RESULTS

### Oxidative Alkaline Leaching of Americium from BiPO<sub>4</sub> Sludge with KMnO<sub>4</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

Because the BiPO<sub>4</sub> sludge has the highest concentration of transuranic elements (TRUs) among all the sludges in the waste tanks, extra efforts were expended in this study on the leaching of americium from the BiPO<sub>4</sub> sludge. Experiments were conducted with two oxidants (KMnO<sub>4</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), three concentrations of NaOH (1, 3, and 5 M, as well as in the absence of NaOH), and at two temperatures (25 and 70°C).

#### Leaching with Potassium Permanganate (KMnO<sub>4</sub>)

The results of the leaching of americium by NaOH in the presence of KMnO<sub>4</sub> from the BiPO<sub>4</sub> sludge are summarized in Table 1. In the absence of KMnO<sub>4</sub>, more than 99% of americium remained on the sludge after leaching with 1–5 M NaOH for 50 h at 25°C ( $K_d = 20,000\text{--}80,000\text{ mL/g}$ ) and 5 h at 70°C ( $K_d = 10,000\text{--}16,000\text{ mL/g}$ ), where  $K_d$  is the distribution coefficient and equal to the ratio of  $[\text{Am}]_{\text{sludge}}/[\text{Am}]_{\text{solution}}$ , in the unit of mL/g. This result is fully consistent with the known chemistry of trivalent actinides in alkaline media. Sorption of Am(III) on the sludges is often nearly quantitative (as indicated in the loading experiments). Furthermore, the hydroxides, fluorides (present in BiPO<sub>4</sub> sludges), and phosphates of Am(III) are known to have very low solubility in neutral to basic solutions (12, 13), hence the intrinsic insolubility of Am(III) in discrete crystalline phases should also inhibit its solubility.

As the data in Table 1 show, introduction of KMnO<sub>4</sub> into the NaOH leachate results in 10–50% of the americium being removed from the sludge relatively quickly. The percentage leached increases with the concentration of NaOH. The net percentage leached is only slightly increased by raising the temperature. In all cases, attainment of a steady state occurred within less than 30 min. If the system is achieving a true steady state in these experiments, this result implies either that Am(III) on the sludge is oxidized to a higher oxidation state [e.g., Am(V)] with higher solubility in alkaline solutions, or that a specific association between Am(III) and a mineral phase that dissolved in alkaline permanganate in this sludge simulant was responsible for Am(III) retention in the sludge sample. We think that the latter scenario is less likely because the Am(III) that has entered the solution phase due to the dissolution of the mineral phase would, if not oxidized to more soluble higher oxidation states, form hydroxides and precipitate out from the solution. The only reasonable explanation for the increased leaching of americium in the presence of KMnO<sub>4</sub> is the oxidation of Am(III), probably to Am(V) that has higher solubility in

**Table 1.** Leaching of americium from BiPO<sub>4</sub> sludge with NaOH/KMnO<sub>4</sub> at 25 and 70°C

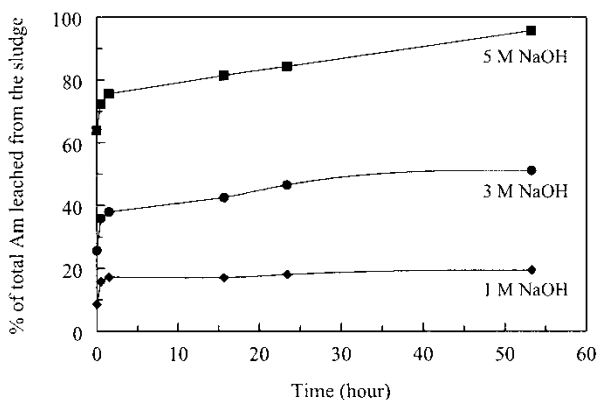
Temperature (°C)	Time (hours)	% Americium in solution					
		1 M NaOH: Without KMnO <sub>4</sub>	1 M NaOH: 0.1 M KMnO <sub>4</sub>	3 M NaOH: Without KMnO <sub>4</sub>	3 M NaOH: 0.1 M KMnO <sub>4</sub>	5 M NaOH: Without KMnO <sub>4</sub>	5 M NaOH: 0.1 M KMnO <sub>4</sub>
25	0.5	0.2	15.6	0.5	37.9	1.2	43.2
	1.0	0.2	14.7	0.3	38.2	0.4	38.3
	3.0	0.2	14.3	0.3	36.7	0.3	39.9
	22.0	0.2	11.6	0.2	33.2	0.4	40.7
	30.0	0.1	11.8	0.2	29.6	0.2	34.7
	44.0	0.1	10.5	0.2	29.4	0.3	38.2
	52.0	0.1	8.6	0.3	35.5	0.4	43.0
70	0.5		18.6		33.4		38.3
	1.0		19.1		38.1		46.9
	3.0		15.0		39.1		48.2
	5.0	0.5	17.2	0.7	34.0	0.8	42.0



alkaline solutions. Unfortunately, the use of very low concentrations of americium in the experiments prohibits a direct determination (for example, by spectrophotometry) of the oxidation state of americium in the leachate. Typical radioanalytical techniques for actinide oxidation state characterization (14) would likewise prove unsuitable because of the strongly oxidizing characteristics of americium in its higher oxidation states.

The color of the leaching solution became so intensely dark after the first washing, probably resulting from a mixture of manganese species [purple  $\text{MnO}_4^-$ , dark green  $\text{MnO}_4^{2-}$ , brown  $\text{MnO}_2(\text{s})$ , etc.] and dissolved sludge matrix components (chromium, iron and rare earths), that it was very difficult to visually identify the presence of excess  $\text{KMnO}_4$ . In the solutions of 3 M and 5 M NaOH, the supernatant after the first washing was actually dark green, indicating the reduction of  $\text{MnO}_4^-$  to  $\text{MnO}_4^{2-}$ .

Since the amount of oxidant (0.1 M) is in large excess with respect to the amount of americium (and other potential oxidizable components) in the sludge, it is not obvious why the amount of americium in the leachate should plateau (at 10–50% leached) and remained unchanged for many hours (Table 1). To provide further insight into the leaching process, a consecutive second batch washing experiment was conducted in this system. The results of the second washing (Fig. 1) indicate that additional americium is leached from the sludge by fresh solutions of  $\text{KMnO}_4/\text{NaOH}$ . In fact, nearly 90% of total americium could be leached by  $\text{KMnO}_4/5\text{ M NaOH}$  with two “fresh” washings. These results suggest that the apparent excess of oxidants might gradually be consumed by other reactions including self-decomposition. There could be many components in the sludge that can catalyze such reactions. These results suggest that, if the



**Figure 1.** Second washing of simulated  $\text{BiPO}_4$  sludge with  $\text{NaOH}/0.1\text{ M KMnO}_4$  (percentage values represent TOTAL amount of americium leached during both washings).

americium is to be retained in the sludge phase when using oxidative alkaline leaching to remove chromium, consecutive leachings should be avoided, as near complete mobilization of americium from the sludge phase could occur. However, if the aim of oxidative leaching became removal of transuranium elements from the sludge, then consecutive oxidative leaching may become an appropriate treatment regimen.

### Leaching with Potassium Persulfate ( $K_2S_2O_8$ )

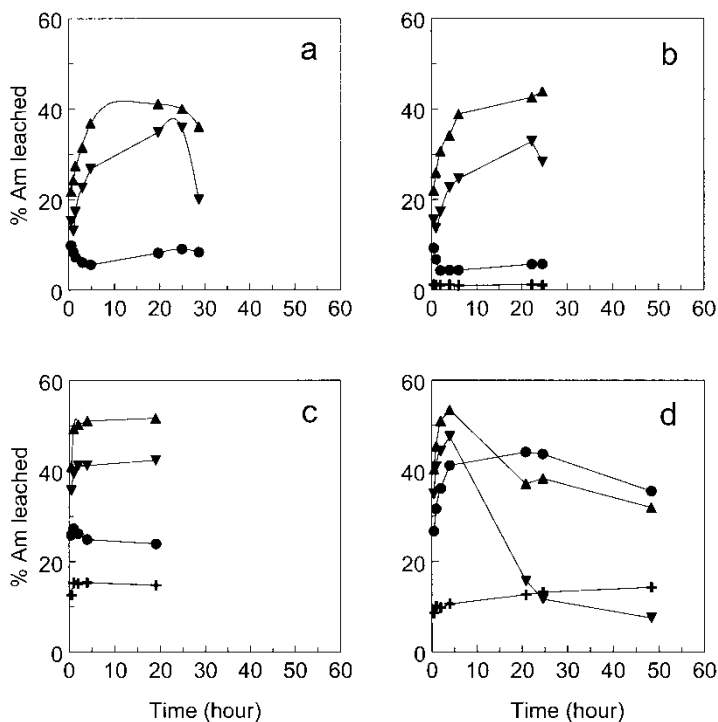
Introduction of persulfate into alkaline solutions (1, 3, and 5 M NaOH) results in patterns of enhanced release of americium from  $BiPO_4$  sludge to the solution (leachate) phase, as shown in Table 2. In the absence of  $K_2S_2O_8$ , less than 1% americium was leached from the sludge, as shown in Table 1. The results in Table 2 can be summarized in the following trends: (1) similar to the leaching with  $KMnO_4$ , higher concentration of NaOH leads to higher leaching of americium with  $K_2S_2O_8$ ; (2) raising the temperature from ambient to 70°C has a minimal effect on the amount of americium leached from the sludge, though the steady-state concentration of americium appears to be achieved more rapidly at 70°C than at 25°C; (3) with 0.1 M  $K_2S_2O_8$  and 3–5 M NaOH, about 40% americium was leached in a few hours.

**Table 2.** Leaching of americium from  $BiPO_4$  sludge with NaOH/ $K_2S_2O_8$  at 25 and 70°C

Temperature (°C)	Time (hours)	% Americium in solution		
		1 M NaOH 0.1 M $K_2S_2O_8$	3 M NaOH 0.1 M $K_2S_2O_8$	5 M NaOH 0.1 M $K_2S_2O_8$
25	0.5	9.9	15.2	21.8
	1.0	8.4	13.1	24.3
	1.5	7.3	17.3	27.5
	3.0	6.1	22.6	31.5
	4.8	5.6	26.8	36.9
	19.7	8.2	34.8	41.1
	24.9	9.1	35.9	40.0
	28.7	8.4	20.0	36.1
70	0.5	10.7	30.7	41
	1.0	10.7	32.0	42.3
	1.5	11.2	32.9	41.7
	3.0	10.4	31.9	35.6

### Oxidative Alkaline Leaching of Americium from Other Sludges with $K_2S_2O_8$ at 25°C

To evaluate the effect of sludge matrix on the leaching of americium, experiments were conducted on other sludges ( $BiPO_4$  modified, Redox, and PUREX) with  $K_2S_2O_8$  at 25°C. The results including those of the  $BiPO_4$  sludge previously described are shown in Fig. 2. Though it is clear that higher concentrations of NaOH lead to greater mobilization of americium from all sludges in the presence of persulfate, different sludges do show distinctively different patterns of leaching with time and NaOH concentration. The results in Fig. 2 clearly demonstrate that the nature of the sludge has a significant impact on the progress of americium leaching.



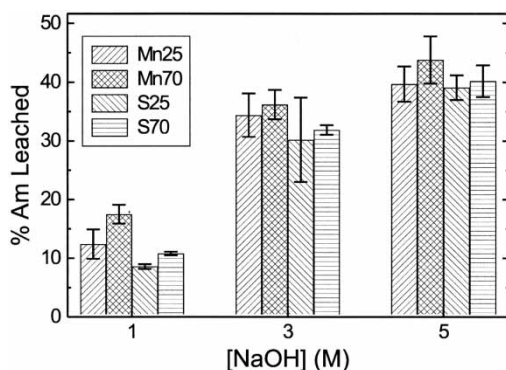
**Figure 2.** Leaching of americium from sludge simulants by 0.1 M  $K_2S_2O_8$  in alkaline solutions: a -  $BiPO_4$  sludge; b -  $BiPO_4$  modified sludge; c - PUREX sludge, d - Redox sludge. Symbols for different leachant: (⊕) 5.0M NaOH, no oxidant present; (●) 1.0M NaOH; (▼) 3.0M NaOH; (▲) 5.0M NaOH.

## DISCUSSION

## Steady-State Leaching Conditions

Leaching from the BiPO<sub>4</sub> Sludge

Having examined the leaching of americium from the BiPO<sub>4</sub> sludge by both persulfate and permanganate as a function of time, [NaOH], and temperature, we have an opportunity to assess the comparative influence of these parameters on americium leaching in this system. These data are shown in Fig. 3. The values plotted in the case of permanganate represent steady-state concentration of americium in the solution phase (which was stable during the 20 h observation period) while the corresponding persulfate data are the maximum concentrations. The increase in temperature appears to have no statistically significant effect on the amount of americium leached in either system. The close coupling of the percent americium leached by the two oxidants strongly suggests that the amount of americium released is governed more strongly by the nature of the solid substrate than the power of the oxidant. It suggests predominance of a mechanism involving disruption of the solid matrix by the oxidant, which releases americium to the solution phase wherein Am(III) is then converted to a more soluble form. Furthermore, the similarity of the results from the two oxidants implies that the products of the reduction of permanganate and persulfate (e.g., MnO<sub>2(s)</sub>, SO<sub>4</sub><sup>2-</sup>) do not impact significantly the solubility of americium in the alkaline wash solution.



**Figure 3.** “Steady-state” americium leaching by permanganate and maximum americium leaching by persulfate from BiPO<sub>4</sub> simulant as a function of [NaOH] and temperature. Symbols: (Mn25) KMnO<sub>4</sub> at 25°C; (Mn70) KMnO<sub>4</sub> at 70°C; (S25) K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> at 25°C; (S70) K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> at 70°C.

### Leaching from Different Sludges

The distinct patterns of americium leaching from the four sludges by  $K_2S_2O_8$  (Fig. 2) must derive in some manner from the differences in sludge composition, whether chemical factors or particle size/surface area mediated. Furthermore, the general similarity of americium leaching from  $BiPO_4$  (Fig. 2a) and  $BiPO_{4\text{ modified}}$  (Fig. 2b) indicates that the substitution of probe atoms (neodymium and europium) has little effect on the leaching of americium. In interpreting these results, it is important to recognize that in these biphasic experiments there are numerous potential pathways by which americium can be mobilized from the sludge samples.

The leaching of americium from the Redox sludge shows the greatest mobilization of americium of any of the four sludge samples in 1 M NaOH (Fig. 2d). The pattern of americium leaching in the Redox sludge system is also distinguished by the rapid decline in the amount of mobilized americium beyond 4 h contact at low base concentration (3 and 1 M NaOH). At the same time, more americium remains in solution for a longer period of time at higher base concentrations (5 M NaOH).

As noted previously, the defining characteristic of the Redox sludge simulant is the content of aluminum (by weight): 25.4% (Redox), 0% ( $BiPO_4$ ),  $\leq 3.9\%$  (modified  $BiPO_4$ ), and  $< 0.2\%$  (PUREX) (8). One possible interpretation of these observations is that americium leaching may be a result of close association between  $Al_2O_3$  and oxidizable components like  $Cr_2O_3$  in the Redox sludge simulant. The alkaline oxidative treatment causes rapid initial disruption of the sludge matrix, mobilizes aluminum and chromium as well as the americium associated with the matrix to the solution phase, and allows oxidation of americium, which remains in the solution phase under an oxidizing condition. The formation of polyaluminate anions, which becomes more likely at high concentrations of aluminate and low base concentrations (15), could lead to the formation of colloids on which americium species could be readily sorbed (16). Re-precipitation of the temporarily dissolved aluminum could account for the comparatively rapid redeposition of americium onto the sludge. The tendency of  $AlO_2^-$  to remain soluble (and monomeric) should increase with increasing [NaOH]; hence the oxidized/mobilized americium remains in the solution phase for a longer period at higher [NaOH] (5 M). A previous study of the leaching of U(VI) from the four sludge simulants (7) indicated that the chemical environments of U(VI) in the sludges are different. Data obtained by Extended X-Ray Absorption Fine Structure Spectroscopy (EXAFS) suggest that U(VI) is probably incorporated into the matrix of  $BiPO_4$  and PUREX sludges but could possibly exist as discrete hydrous oxides in the Redox sludge. The low americium concentration used in the present work does not allow the characterization of americium in the sludges by EXAFS. However, the distinct differences in the rate of leaching of americium from the  $BiPO_4$

sludges and the patterns of “redeposition” in the leaching from the Redox sludge support the hypothesis that Am(III) is associated with phosphate in the BiPO<sub>4</sub> sludges but is either associated with aluminate or present as hydroxide in the Redox sludge.

### Leaching Kinetics and Possible Mechanisms

Data in Fig. 2 indicate that, qualitatively, the rates of americium leaching increase in the order BiPO<sub>4</sub> < Redox < PUREX sludges. Since the oxidant and the hydroxide are in large excess of americium, the reactions in this study were treated as pseudo first-order reactions, where the rate =  $k_{\text{obs}}[\text{Am(V)}]$ .

If we take the maximum percent leached in each plot as  $A_{\infty}$  and format the data as  $(A_{\infty} - A)$ , a semilogarithmic plot of  $(A_{\infty} - A)$  as a function of time conforms to a linear relationship, indicating that an apparent first-order rate process describes the release of americium from the sludge samples. For the PUREX samples, a limiting slope was determined; that is, a slope was calculated using the first two data points. For the other sludge samples, each curve was characterized by three to five experimental points. The resulting rate constants are shown in Table 3. The derived rate constants for BiPO<sub>4</sub> and BiPO<sub>4</sub> modified experiments overlap at the  $\pm 3\sigma$  uncertainty level at 3 M and 5 M NaOH, confirming that the modification has no significant impact on the rate of americium leaching by persulfate. In 3 M NaOH, the rates of release of americium from the PUREX sludge is twice that from the Redox sludge, which is in turn four to five times faster than that seen from the BiPO<sub>4</sub> sludge. Each sludge demonstrates a slightly different dependence on the base concentration, the effect being most pronounced in the PUREX sludge while the leach rate from the BiPO<sub>4</sub> sludge is nearly independent of [NaOH].

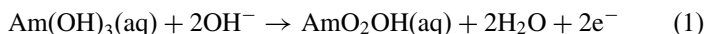
Assuming that americium dissolution is a result of its oxidation (rather than specific mineral association), the possible oxidation states are Am<sup>4+</sup>,

**Table 3.** Pseudo first-order rate constants for americium leaching from sludge simulants by alkaline persulfate solutions (0.1 M persulfate). (Uncertainties represent 95% confidence interval, no uncertainties are indicated for PUREX results because these are limiting rates calculated from two experimental data points.)

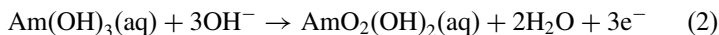
Sludge	1.0 M NaOH $k_{\text{obs}}$ (h <sup>-1</sup> )	3.0 M NaOH $k_{\text{obs}}$ (h <sup>-1</sup> )	5.0 M NaOH $k_{\text{obs}}$ (h <sup>-1</sup> )
BiPO <sub>4</sub>	—	$0.16 \pm 0.04$	$0.34 \pm 0.05$
BiPO <sub>4</sub> modified	—	$0.21 \pm 0.05$	$0.25 \pm 0.04$
Redox	$0.50 \pm 0.03$	$0.89 \pm 0.28$	$1.14 \pm 0.10$
PUREX	—	1.64	3.07

$\text{AmO}_2^+$ , and  $\text{AmO}_2^{2+}$ . In acidic solutions, all three of these species are powerful oxidants with potentials decreasing in the order  $\text{Am}^{4+} > \text{AmO}_2^{2+} > \text{AmO}_2^+$ . Redox potentials for americium in alkaline solution have not been measured. By analogy with other tetravalent actinides ( $\text{Th}^{4+}$ ,  $\text{U}^{4+}$ ,  $\text{Pu}^{4+}$ ,  $\text{Np}^{4+}$ ),  $\text{Am}^{4+}$  should exhibit low solubility in alkaline solutions; hence its presence in the solution phase in the absence of solubilizing complexants (e.g., EDTA) is considered unlikely. We are left to conclude that either  $\text{AmO}_2^+$  or  $\text{AmO}_2^{2+}$  (or both) are present in the solution phase (presumably as hydroxide complexes) while the solution remains under oxidizing conditions. Our prior work on neptunium speciation (17) has established the comparative redox stability and solubility of the respective tetrahydroxides of penta- and hexavalent actinides in concentrated base solutions.

The exact reaction pathway(s) and mechanism of the oxidation/solubilization reactions are not clear from these experiments due to the complexity of the americium species in basic media and that of the sludge simulant samples. However, if we assume the hydroxides,  $\text{Am}(\text{OH})_3$  and  $\text{AmO}_2\text{OH}$ , are dominant, the oxidation of  $\text{Am}(\text{OH})_3$  to  $\text{AmO}_2\text{OH}$  in basic media can be represented by reaction 1:

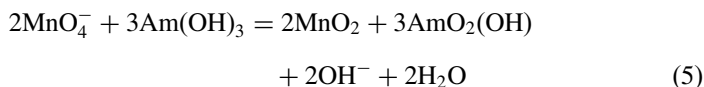
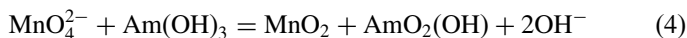


A standard potential (1.0 M NaOH) for reaction 1 has been calculated ( $E^\circ = -0.5 \text{ V}$ ) based on standard potentials in 1.0 M acid ( $E^\circ = -1.72 \text{ V}$ ) (18) but no experimental exists. Reaction 2 indicates that higher concentrations of NaOH would facilitate the oxidation of  $\text{Am}(\text{OH})_3$  to  $\text{AmO}_2(\text{OH})_2$ .



The estimated potential value for reaction 2 is  $-0.6 \text{ V}$  (18). It should be noted that we cannot eliminate the possibility of anionic species being present in solution, such as  $\text{AmO}_2(\text{OH})_n^{-(n-1)}$  (where  $n = 1 - 4$ ), which have been found to be stabilized under increasing hydroxide concentrations (19).

If one considers the net thermodynamic equilibrium for the manganese-amerium system in concentrated basic solutions [assuming  $\text{Am}(\text{V})$  as the probable product], the following possible equilibria are obtained (all are for aqueous systems):



Reaction 3 [for  $\text{Mn}(\text{VII})/\text{Mn}(\text{VI})$ ] is favored by excess base, consistent with the observation that the  $\text{Mn}(\text{VII})/\text{Mn}(\text{VI})$  reaction was complete

within 24 h in 3 M NaOH (identified visually by the color change from purple to green), but much slower in 1 M NaOH. On the contrary, reactions 4 and 5 ending in  $\text{MnO}_2$  are inhibited by excess base. We speculate that the initial mobilization of americium from the sludge phase is a result of a process like that described by reaction 3, thus favored by increased concentration of base. With time, the importance of this reaction decreases as  $\text{MnO}_4^-$  is converted to  $\text{MnO}_4^{2-}$  with further changes inhibited by a kinetic barrier to further reactions such as dissolution and structural rearrangements.

Potassium persulfate is known to be a strong oxidant in basic solutions, though one with significant kinetic limitations. Previous studies (20–23) suggest that intermediate products ( $\text{SO}_4^-$  and  $\text{HS}_2\text{O}_8^-$ ) rather than persulfate itself are responsible for oxidation under most conditions. The primary reduction reaction (24),



is pH independent in neutral-alkaline solutions, hence the thermodynamic oxidizing power should not change with pH. However, it is known that strong bases cause the catalytic decomposition of  $\text{S}_2\text{O}_8^{2-}$  (25), hence higher concentrations of more reactive species may be available at higher [NaOH] leading to possible significant differences in kinetic behavior. Noble metals ( $\text{Ag}^+$  in particular) are known to catalyze persulfate oxidation, probably through the creation of unstable intermediates like  $\text{Ag}^{2+}$ . As silver, palladium, and rhodium are fission products of significance and certainly present in tank wastes, such catalytic reactions might assume an important role during persulfate oxidation of actual sludges, though these metals are not present in the simulant sludge samples in this study.

Though “kinetically challenged,” the persulfate system has an adequate thermodynamic driving force to accomplish the oxidation of both Cr(III) and Am(III) readily (see reaction 6). The net reaction for americium oxidation is:



The thermodynamics of this reaction are such that increased base concentration should promote oxidation of Am(III). This is consistent with the observed behavior of the system shown in Fig. 2, where higher concentration of NaOH results in a higher percentage of americium leached. The decline in americium leaching observed beyond 20 h in the Redox samples most probably reflects the formation of aluminate colloids and the redeposition of americium on the solid phase as discussed previously.

One particularly interesting aspect of this study is the plateauing that is observed in the mobilization of americium to the leachant phase. The faster initial rate is believed to be attributable to the reaction of the oxidant with the americium, which is probably sorbed on the surface of the sludge. The plateauing may then be due to a process controlled by the diffusion of the



solubilized americium species into the pores of the sludge. Based on the results of the secondary washing experiments, we assume that the oxidants may be consumed by processes such as self-decomposition catalyzed by various sludge components. However, a more satisfactory explanation may require conducting experiments with macro-amounts of americium so that the oxidation state of americium can be directly determined by other techniques including UV/Vis/IR spectroscopy and EXAFS.

## CONCLUSIONS

1. Significant amounts of americium were leached from the simulated HLW sludges by  $\text{KMnO}_4$  and  $\text{K}_2\text{S}_2\text{O}_8$  in alkaline solutions. The enhancement of leaching is believed to be due to the oxidation of Am(III) to Am(V). The increase of temperature has little effect on the percentage of americium leached, but does significantly increase the rate.
2. Higher concentrations of NaOH (from 1 to 5 M) facilitate the leaching of americium in the presence of  $\text{KMnO}_4$  and  $\text{K}_2\text{S}_2\text{O}_8$ .
3. The rate of leaching is dependent on the sludge matrix and composition. The relative rates of dissolution of americium from the sludge simulants increase in the order  $\text{BiPO}_4 < \text{Redox} < \text{PUREX}$ . Under similar conditions, slightly less americium is leached from the  $\text{BiPO}_4$  sludges than the Redox and PUREX sludges. It is believed that the chemical environments of americium in the sludges may account for this difference: the americium is probably associated with phosphate in the  $\text{BiPO}_4$  sludges while existing as hydrous oxide in the Redox and PUREX sludges.
4. There is a pronounced tendency for dissolved americium to be redeposited in the Redox system at low base concentration, probably related to limited solubility of  $\text{NaAlO}_2$  and its tendency to polymerize and remineralize at low base concentrations.
5. Alkaline oxidative leaching with  $\text{KMnO}_4$  and  $\text{K}_2\text{S}_2\text{O}_8$  could remove some americium from the sludge. As a result, it should be used with caution when the objective of sludge washing is to remove Cr from the sludge while keeping actinides in the sludge. Further studies are needed to evaluate the options of using "milder" oxidants or applying kinetic control so that Cr can be effectively removed with actinides remaining in the sludge. These studies are beyond the scope of this work.

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