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Oxidative Leaching of Plutonium from Simulated Hanford Tank-Waste Sludges

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Abstract: The behavior of surface-sorbed plutonium during leaching of four Hanford tank waste sludge simulants with alkaline permanganate solutions has been investigated. The sludge simulants are representative of materials created as a result of the operation of the Bismuth Phosphate (sludges B and M), PUREX (sludge P), and REDOX (sludge R) processes at Hanford. Leaching with oxidants under alkaline conditions has been proposed as a means of reducing the chromium content of actual sludge samples prior to their vitrification. With identical amounts of plutonium deposited on each sludge sample, the percentage of radiotracer Pu leached from the sludges increased in the order $P \geq R > B$. This order is the reverse of the chromium content of the sludges. The percentage of plutonium leached was independent of its initial oxidation state. The reverse trends of chromium content and plutonium leaching can be understood in terms of Pu re-adsorption onto the MnO_2 generated as Cr(III) (and other substrates) are oxidized by permanganate/manganate. The effect of chelating agents that are known to be present in tank wastes (EDTA, gluconate, glycolate, oxalate, and citrate) on $KMnO_4$ reduction/MnO_2 production and redeposition of plutonium was also studied and found to have varied effects on the process of oxidative dissolution/Pu redeposition. Overall, it appears that the MnO_2 produced as a byproduct of oxidation helps to control Pu concentrations in the leachate phase. Oxidation of Pu to the hexavalent state without concomitant production of MnO_2 leads to greater plutonium content in the leachate. The results are discussed, emphasizing the potential impact of oxidative leaching on plutonium mobilization from actual tank-waste sludge.

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INTRODUCTION

During more than 40 years of plutonium production at the Hanford site, considerable quantities of radioactive byproduct materials were generated (resulting from the application of several different separations/purification processes) and stored (after treatment to stabilize the wastes and reduce corrosion) in underground waste tanks of concrete and steel construction. The waste materials have their origins in a variety of different chemical separations processes and so are characterized by a range of compositions. Further complicating the composition of individual tanks, materials were pumped from tank to tank and subject to evaporation. During 40+ years of storage in the tanks, the wastes have experienced continuous radiolysis and in many cases elevated temperatures. This diversity and complexity is one of the principal obstacles to cleanup of the tanks.

In each case, the alkaline materials in 177 underground waste tanks at the Hanford site have stratified over the years of storage to produce a layered mix of salt-cake, slurry, and sludge, in order of increasing density. The former (containing much of the fission product cesium and technetium) is primarily composed of sodium salts (nitrate, hydroxide, carbonate), while the latter (containing fission product strontium, rare earths, and transuranic elements) consists principally of metal oxides and hydroxides. The radioactive components of the wastes represent less than 1% of the total mass of materials in the tanks, but in most cases the greatest hazard and the most demanding obstacle to environmental cleanup. To remediate these wastes, the salt cake and slurry phases will be removed and treated with relative ease. The sludge phase will be retrieved and treated with considerably greater difficulty.

The high-level radioactive wastes represented by the sludge phase are destined to be immobilized in borosilicate glass and cast into stainless steel canisters prior to geologic disposal. Because the radioactive components represent only a small fraction of the total volume/mass of tank sludge, there is considerable economic and safety incentive to remove as much of the nonradioactive components as possible prior to vitrification. Caustic leaching is expected to be the baseline method for pretreating the sludges (1). The purpose of this treatment is to remove those materials either readily recycled (or suitable for near-surface disposal or other disposition pathways) or incompatible with the glass formulation. Aluminum, chromium, sulfur, and phosphorus are poorly tolerated in borosilicate glass or are problematic in the vitrification process. Each is in principle removable from the sludge in an alkaline scrub.

The chromium concentration in the high-level fraction of Hanford tank sludges has the strongest influence on the volume of immobilized glass wastes (2, 3). Therefore minimizing the amount of residual chromium in the sludge is an important pretreatment objective. Trivalent chromium is far less soluble than the oxidized species in strongly basic solutions, particularly at elevated temperatures (4). Rai and coworkers have suggested a thermodynamic model for the prediction of Cr(III) solubility from amorphous $Cr(OH)_3$ in concentrated NaOH solutions (5). Addition of an oxidant capable of converting Cr(III) to Cr(VI) (to enhance its dissolution from the sludge phase (6)) is being evaluated as a supplemental treatment option.

Rapko, Lumetta, and coworkers (PNNL) have conducted the most extensive series of studies of oxidative leaching for Cr removal from actual Hanford tank sludges and simulants (4, 6–8). They have reported that:

- H_2O_2 is ineffective in concentrated alkali, probably due to iron catalysis of its decomposition.
- O_3 is rapid and effective but enhances dissolution of TRU elements and is excessively corrosive to the walls of the tanks.
- O_2 is effective and selective, but slow—no enhancement in dissolution of radionuclides was noted but 2 weeks' contact would be needed for practical application.
- Persulfate is effective for several Cr mineral phases, but oxidizes TRU's and introduces sulfate into the Low-Activity Waste stream.
- Ferrate is rapid and effective, mobilizes little TRU, but is unstable (as compared with permanganate) and thus would be challenging to use at large scale.
- Permanganate is rapid and effective, exhibits little TRU dissolution at low hydroxide concentration, but produces MnO_2, which may either be deleterious or helpful depending on the feed composition.

Rapko (7) observes that with permanganate "1 hour contact is adequate for Cr oxidation/dissolution," and concludes that of the several oxidants considered ". . . only permanganate treatments removed sufficient Cr to reduce the Cr concentration of the leached sludges as the limiting factor in waste oxide loading of the ILHW glass."

Dissolution of actinides from the sludge phase into a mobile liquid phase is considered an undesirable outcome of sludge leaching, as the residues constitute feedstock for the HLW glass melters. Though the PNNL work appears to indicate that permanganate may be capable of selective Cr oxidative leaching without actinide mobilization, the potentials are such that actinide oxidation cannot be ruled out under all circumstances. The inherent complexity of sludge wastes suggests that these few observations, while promising, are not adequate to ensure that TRUs will not be mobilized from tank sludges under all conditions that might be encountered during oxidative alkaline leaching. Furthermore, literature reports of actinide chemistry in strongly alkaline solutions are limited in nature and scope, and so assurance of performance through computational modeling of actinide behavior in alkaline sludge leaching based on thermodynamic data is not practicable.

In this work, the behavior of sorbed plutonium (initially either Pu(IV) or Pu(VI)) during the leaching of four previously characterized sludge simulants [Bismuth Phosphate (B), Modified Bismuth Phosphate (M), Purex (P), and REDOX (R) (9)] with alkaline permanganate has been investigated. The effect of permanganate concentration and of selected water-soluble chelating agents on the reduction of $KMnO_4$ and on plutonium mobilization also has been studied.

EXPERIMENTAL

Sludge Preparation and Leaching

Four simulated sludges (B, M, P, R as defined previously) were prepared at Argonne National Laboratory based on the formulae reported by Kupfer (10). The modifications to the M sludge sample consist of the substitution of 1/3 Nd, 1/3 Eu, and 1/3 La for the La fraction (Nd and Eu can be characterized using various spectroscopic techniques that provide no useful information for La alone), and the introduction of small amounts of Ti, Al, and Fe to simulate their presence in actual sludge samples. Detailed information on the composition of the sludge simulants has been provided in an earlier report (8). Selected portions of the prior sludge simulant analysis are reproduced in Table 1.

Because the $BiPO_4$ process relied on coprecipitation of actinides in $BiPO_4$ and LaF_3 solid phases, these sludge simulants are dominated by these species and lanthanide phosphates. Our prior analysis indicated that the simulant samples (both B and M) contained 5.3–7.6% by weight Cr, 7.2% Mn, and minimal Fe. The REDOX sludge, derived from the effluents of solvent extraction from concentrated $Al(NO_3)_3$ solutions, is dominated by Al_2O_3, but also contains 3.8% Cr, 5.1% Fe, and 1.1% Mn. The PUREX sludge simulant is primarily oxides of iron with lesser amounts of Al_2O_3, 0% Cr, plus 2.2% Mn. Each simulant also carries 12–16% Na.

Chemicals and Equipment

Deionized water from a MilliQ system was used to prepare all solutions. NaOH, HNO_3, HCl, and $KMnO_4$ were of reagent grade and used as received. ^{238}Pu was selected as the appropriate Pu isotope for this study because its high specific activity (3.8×10^7 dpm/μg) allowed us to conduct these experiments at Pu concentrations well below the solubility limits of plutonium. The radiotracer was obtained from the ANL inventory. The oxidation state of the plutonium

Table 1. Analyses of bulk constituents in radioactive waste sludges

	Waste analysis wt%		
Component	$BiPO_4$	REDOX	PUREX
Al + Fe	1.4		
Al		25.4	7.4
Fe		5.1	23.6
Bi	23.6	—	
Ca	—	1.5	1.6
Cr	5.3	3.8	0
La	10.5	—	—
Mn	7.2	1.1	2.2
Na	11.8	15.8	12.2
Ti	1.7		
Si + Ti		6.2	
Si + Ti + Zr			4.9
Anions	12.0	0.5	1.7
Volatiles	14.3	21.0	25.3
O_2	12.2	19.6	21.1

stock solution was alternately adjusted to a predominantly reduced condition (Pu(III/IV)) by treatment with iodide or to a predominantly oxidized condition (Pu(V/VI)) by careful fuming in perchloric acid. All assays of plutonium samples were conducted by liquid scintillation counting.

Experimental Protocol—Leaching Studies

For the leaching studies, 140 mg samples of damp sludge simulants were accurately weighed into polypropylene vessels. Into separate sludge samples, either oxidized or reduced Pu was introduced from dilute sodium bicarbonate solution. Both oxidized and reduced Pu partitioned predominantly to the sludge simulant ($>95\%$) within a few hours equilibration time with gentle mixing. The total plutonium activity in each experiment was approximately 60,000 dpm α (about 0.03 μCi). The loading solution was carefully decanted, assayed to determine uptake and discarded. In the leaching experiments, 2.0 mL leachant solution was introduced and the samples were gently mixed at room temperature for 1 h prior to sampling of the leachate. Quantitative leaching of the Pu tracer into the leachant would produce a solution of 3×10^{-9} M (5×10^5 Bq/L–14 μCi/L) ^{238}Pu.

In the baseline alkaline leaching studies, 2.0 mL of 3.0 M NaOH with variable [$KMnO_4$] (between 10^{-5} and 0.1 M) was employed as the leachant. The Cr(VI) concentration generated as a result of leaching was determined spectrophotometrically (as permitted by permanganate/manganate spectral interferences, discussed next). The leachates were analyzed radiometrically for their Pu content with samples taken before and after filtration.

As organic complexants are present in some tank wastes and these materials are expected to be susceptible to oxidative degradation, we also examined the impact of the presence of selected water-soluble complexants on plutonium concentrations in alkaline oxidative leachates. We elected to study citrate, oxalate, gluconate, glycolate, and ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA). Each of these complexants either are known to be present in tank wastes or to have been used during plutonium production and subsequently disposed to the tanks in process effluents. The purpose of these experiments was threefold: 1) to determine what effect the simultaneous presence of organic complexants and permanganate might have on plutonium dissolution from sludge simulants into strongly alkaline solutions, 2) to learn the degree to which permanganate might be consumed in the oxidation of organics, and 3) to assess the potential for byproduct MnO_2 to reduce plutonium concentrations in the leachate phase. These experiments were conducted in the absence of sludge simulants. Using this approach, it was expected that the Pu would remain in the solution phase (through the combined action of the complexants and the oxidant) unless the MnO_2 generated by oxidation of the organics sorbed this material from the solution phase. Sorption of actinides onto MnO_2 has been reported (11–14).

In these experiments, the oxidative leaching solution 0.1 M $KMnO_4$ in 3 M NaOH was mixed with the aliquots of each organic compound at varying stoichiometric ratios of complexant to oxidant. The solutions were vigorously agitated by vortex mixing from 1 to 4 h at room temperature, which we determined was an adequate time to allow the system to reach a steady state. The concentration of permanganate was determined spectrophotometrically, while Pu was assayed radiometrically by liquid scintillation.

RESULTS AND DISCUSSION

Leaching of Chromate

Potassium permanganate in strongly basic solutions is slowly converted into potassium manganate. At least one report implies that this conversion is catalyzed by transition metal impurities (15). The reduction potential E^0 of MnO_4^-/MnO_4^{2-} is +0.56 V (16), strong enough to oxidize hydroxide in alkaline solutions ($O_2 + 2H_2O + 4\ e^- \rightarrow 4\ OH^-$) $E^0 = +0.401$ V at pH ~14 (17). Though manganate is often referred to as being stable in basic solutions, the reduction potential for Mn(VI)/Mn(IV) (1 M NaOH) is +0.62 V (16), hence it is thermodynamically as potent an oxidant as permanganate under these conditions. Its stability is therefore based on the kinetic features of its reactions.

The changes of the UV-visible spectrum of permanganate in 3 M NaOH solution as a function of time are presented in Fig. 1. It can be seen that the 520 nm band of permanganate slowly disappears while a new band with $\lambda_{max} = 610$ nm assigned to manganate grows in. The well-shaped isosbestic point at 580 nm can be used for determination total manganese content, that is, the sum of manganate and permanganate in the solution. Quantitative conversion of the 0.1 M $KMnO_4$ solution from Mn(VII) to Mn(VI) in basic solutions is reported to require several days, though our observation is that this process is more than 90% complete within less than 24 h in 3 M NaOH. In the absence of readily oxidizable substrates, we have observed that Mn(VI) demonstrates moderate (kinetic) stability in 3 M NaOH (solutions were stable, as indicated by the absence of MnO_2 solid, for up to 1 week).

Manganate has two other absorption bands at 360 and 440 nm that unfortunately overlap with the band of chromate at 372 nm (Fig. 2). Our previously reported results indicate a spectral signal in this wavelength region in 3 M NaOH leaching (without oxidant present) for the PUREX sludge, which is prepared without the addition of Cr in either oxidized or reduced form. The identity of this species remains uncertain at this time, though the high concentration of Fe(III) in PUREX sludge simulant suggest soluble ferric hydroxides as the most reasonable candidate. Another possible candidate is nitrate, though minimal nitrate was expected to remain in the sludge simulant samples. Because of the spectral overlap of the 372 nm band with manganate, it was not possible to monitor directly (by spectrophotometry) the leaching of chromium from the four synthetic sludge samples throughout the range of permanganate concentrations (particularly into 0.1 M $KMnO_4$). Instead, the leaching of chromium was studied as a function of permanganate concentration. While permanganate was present in amounts sub-stoichiometric to the

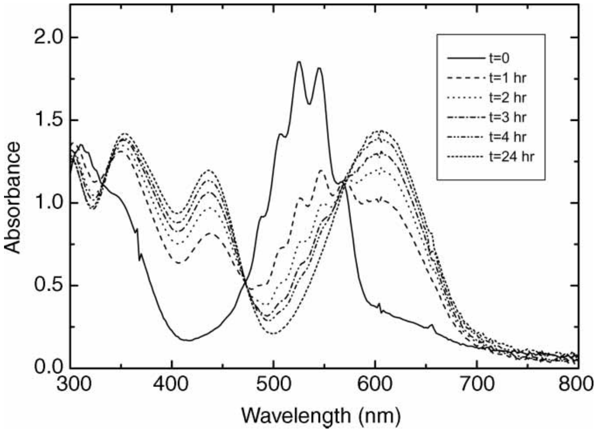

Figure 1. UV-Visible spectral changes for permanganate conversion to manganate as a function of time in 3.0 M NaOH.

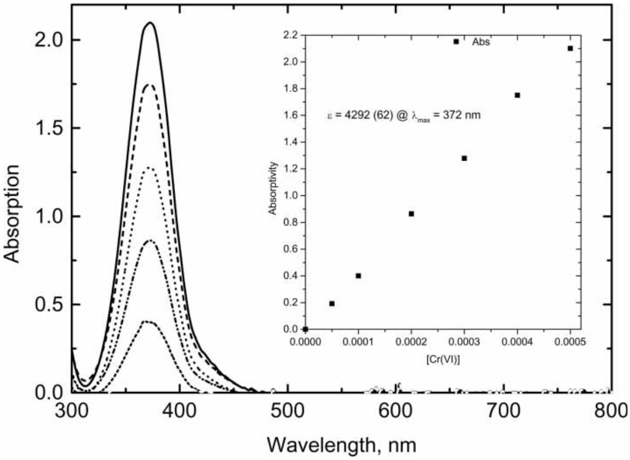

Figure 2. UV-Visible spectra of solutions of variable concentrations of Cr(VI) in 3.0 M NaOH.

chromate present, the supernatant after contact was colorless, implying that MnO_4^- was completely reduced to MnO_2 rather than the MnO_4^{2-} (manganate) intermediate species. The results of these experiments are presented in Fig. 3.

For the lowest concentrations of $KMnO_4$, (less than or equal to 10^{-3} M), chromium leaching from the B, M, and R sludge simulant samples was nearly identical with that observed under the influence of 3 M NaOH in the absence

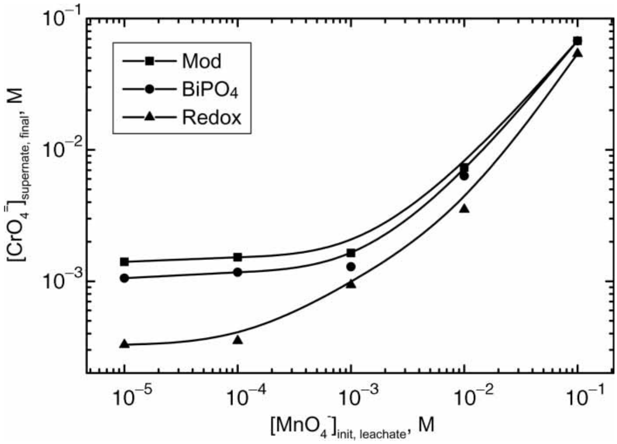

Figure 3. Chromate concentrations in the leachate from oxidative alkaline leaching of Bismuth Phosphate and REDOX sludge simulants at 3.0 M NaOH and variable concentrations of permanganate.

of permanganate. This represents less than 2% of the total Cr present in each sludge sample. Under these conditions, the total oxidizing capacity of the permanganate is well below that required for complete oxidation of all of the Cr present in the sludge simulants (2 mL × 0.001 mmol/mL × 3 meq/mmol = 0.006 meq [assuming 100% Mn(VII) is present intially and that MnO_2 is the ultimate product] vs. 0.038 [Cr wt fraction REDOX] × 140 mg/52 g/mol × 3 eq/mol = 0.31 meq or 0.057 [wt fraction $BiPO_4$] × 140 mg/52 g/mol (Cr) × 3 eq/mol = 0.46 meq). These concentrations of Mn(VII) are well above that required for complete oxidation of ^{238}Pu(IV) to ^{238}Pu(VI) (3×10^{-9} mol/L × 2 eq × 0.002 L = 1.2×10^{-8} meq). As will be described in the following section, Pu leaching responds only minimally to the presence of low concentrations of permanganate.

A significant increase of chromate concentration in the leachate was observed for 0.01 M permanganate. The relative order of chromate concentrations in the leachate was consistent with the known chromium content in the various actual sludges and in our sludge simulants. Because we did not measure the chromate concentration at 0.1 M $KMnO_4$ (as noted previously), the points on the curve at the highest permanganate concentration represent absorbances of chromate in the leaching solution calculated assuming quantitative oxidation and dissolution of Cr under the same analytical conditions. At 0.1 M $KMnO_4$, a stoichiometric excess of Mn(VII) is present relative to the known amounts of Cr(III) present in the REDOX and Bismuth Phosphate sludge simulants (assuming MnO_2 as the ultimate product). Extrapolation of plots in Fig. 3 to 0.1 M $KMnO_4$ suggests that chromium leaching could be almost quantitative by 3 M NaOH containing 0.1 M $KMnO_4$. This result is consistent with the results reported by Rapko in studies of actual sludge samples (7).

Leaching of Plutonium

The behavior of plutonium during the oxidative caustic leaching of all four synthetic sludges was studied under the same analytical conditions as for the chromium oxidative leaching. Separate experiments were conducted with the plutonium sorbed onto the sludge samples initially in either the tetravalent or hexavalent oxidation states. The results of these experiments are presented in Fig. 4. Uncertainties in the percent leached reflect the degree of agreement between duplicate radiometric assay samples at two different initial oxidation states of the Pu. The percent of plutonium removed from the sludge simulant to the leachate proved to be independent of the initial oxidation state of the plutonium. Furthermore, significantly enhanced plutonium leaching under the influence of permanganate was observed only for concentrations of $KMnO_4$ higher than 0.01 M, a behavior that parallels that of the Cr leaching. At 0.1 M $KMnO_4$ the percentage Pu leached

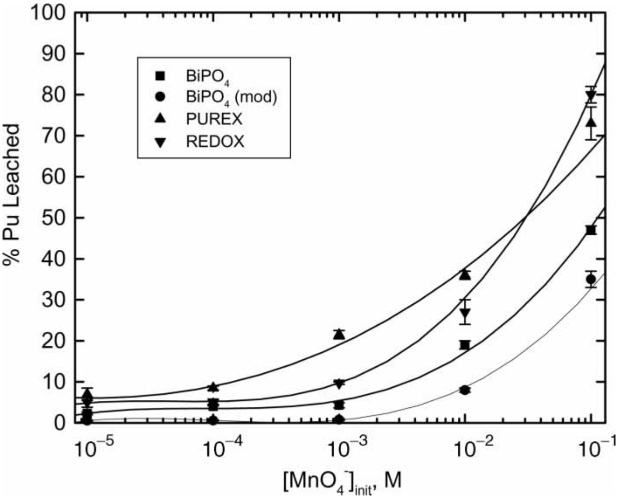

Figure 4. Percentage of sorbed plutonium leached from $BiPO_4$, $BiPO_4$ modified, REDOX, and PUREX sludge simulants into 3.0 M NaOH/permanganate solutions as a function of permanganate concentration.

approaches nearly 80% for PUREX and REDOX type sludges, 45% for bismuth phosphate and 35% for the modified bismuth phosphate.

The thermodynamically stable plutonium species expected in contact with concentrated base (in the absence of strong oxidants) is Pu(IV), most commonly either as highly insoluble PuO_2, $Pu(OH)_4$ or surface-sorbed metal ions (also hydrolyzed). Hydroxides and oxides of Pu(IV) exhibit only very slight solubility in strongly basic solutions. It is therefore anticipated that the plutonium must be oxidized to the more soluble hexavalent oxidation state (Pu(VI)) to be appreciably dissolved into concentrated alkali (Pu(V) would also be more soluble, but its relative REDOX stability is at a maximum in pH 7–9 solutions at low concentrations and declines at both higher and lower pHs). Permanganate is a sufficiently strong oxidant to promote conversion of Pu(IV) to Pu(VI) in strongly alkaline solutions (the reduction potential for (Pu(IV)/(VI)) at pH 14 is +0.34(±0.12)V (18)).

The close parallel between sorption properties of Pu(reduced) and Pu(oxidized), and the lack of an effect of low concentrations of permanganate on Pu mobilization suggests that Pu remains associated with the sludge phase until disruption of the sludge matrix (in this case resulting from Cr(III) oxidation) either promotes its access to permanganate or removes sorptive mineral surfaces (under no circumstances did we observe complete dissolution of the sludge samples). The lower percentages of Pu removed from the $BiPO_4$ and B_m simulants could indicate the impact of the low solubility of lanthanide, bismuth, and Pu phosphates or fluorides relative to the oxide components that dominate the P and R sludge simulants (though coprecipitation of Pu(VI) would have less impact). The sorption of Pu by MnO_2 could also play a role, as this simulant has the highest Mn content (see Table 1).

Sludges containing a greater amount of chromium will consume more oxidant for solubilization of chromium and simultaneously produce more MnO_2. One should therefore expect that the plutonium concentration in the leachate should be lower for chromium rich sludges due to the greater tendency toward redeposition of plutonium on MnO_2 generated in this process. The observation of higher leachate concentrations of Pu in the PUREX sludge is consistent with this interpretation, as the absence of appreciable concentrations of oxidizable species provides no clear avenue toward the production of MnO_2. It is clear that oxidized manganese species could have a substantially similar effect upon encountering any other readily oxidizable substrate (aside from Cr(III) within tank sludges). It is furthermore reasonable to propose that higher concentrations of Pu will be observed in leachant solutions containing an excess of permanganate/manganate, as Pu oxidation will become more efficient under such conditions.

We have recently completed an investigation of the leaching behavior of Am(III) from these same sludge simulants by alkaline permanganate and persulfate (19). We have noted in that system that the rate of oxidative leaching of Am increases in the order $BiPO_4$ <REDOX <PUREX, and that the maximum percentages of leached Am generally parallel the observations we have made in this investigation. Enhanced leaching of Am is likely to be a less persistent feature of alkaline oxidative leaching, as the Am(V) or Am(VI) leached is far more readily rereduced to the trivalent state than Pu.

Effect of Organic Complexants on Reduction of $KMnO_4$ and Pu Sorption

Aside from oxidation, reduced Pu could be mobilized from the sludge to the solution phase under the influence of water-soluble chelating agents, which are known to be present in some waste tanks. In selected tanks known to contain chelating agents, elevated concentrations of actinides in liquid/slurry phases have been reported. Many of these reagents should also be susceptible to oxidative degradation by Mn(VII/VI) species in strong alkali. The possible combined effects of chelation and oxidative degradation (with concomitant production of MnO_2) could have interesting and important implications for actinide chemistry during sludge leaching. The combined effect of organic chelating agents (EDTA, gluconate, glycolate, oxalate, and citrate) on $KMnO_4$ reduction in alkaline medium, the MnO_2 production and the sorption of plutonium was studied with this potential complexity in mind.

In parallel with permanganate oxidation of the organic complexants, sorption of ^{238}Pu under the same experimental conditions was studied. The percentage of plutonium sorbed (to the MnO_2 byproduct) was determined radiometrically, monitoring the difference between initial and final activity of ^{238}Pu in each solution. The results of plutonium sorption are reported in Fig. 5. The plutonium sorption was most efficient and very similar for EDTA and gluconate reaching 85% for concentration of the organics 0.02 M and above. The same level of sorption of Pu was reached at 0.05 M glycolate (in 0.1 M $KMnO_4$/3.0 M NaOH). It is noteworthy that excess EDTA or gluconate (relative to the permanganate consumed) did not result in remobilization of Pu from the MnO_2. In contrast, negligible sorption of plutonium was observed in the presence of oxalate and citrate. In these systems, permanganate was not consumed. It appears that oxalate and citrate are resistant to oxidation by alkaline permanganate/manganate solutions under these conditions.

Thermodynamically, complete oxidation (mineralization) of the organic complexants should be governed by the following half reactions:

$$\text{oxalate: } C_2O_4^{=} + 4O^{H} \rightarrow 2CO_3^{=} + 2H_2O + 2e^- \qquad (1)$$

$$\text{glycolate: } C_2H_2O_3^{-} + 9OH^- \rightarrow 2CO_3^{=} + 6H_2O + 6e^- \qquad (2)$$

$$\text{citrate: } C_6H_5O_7^{3-} + 27OH^- \rightarrow 6CO_3^{=} + 16H_2O + 18e^- \qquad (3)$$

$$\text{gluconate: } C_6H_{11}O_7^{-} + 33OH^- \rightarrow 6CO_3^{=} + 22H_2O + 22e^- \qquad (4)$$

$$\text{edta: } C_{10}H_{12}N_2O_8^{4-} + 50OH^- \rightarrow 10CO_3^{=} + 28H_2O + 2NH_3 + 34e^- \qquad (5)$$

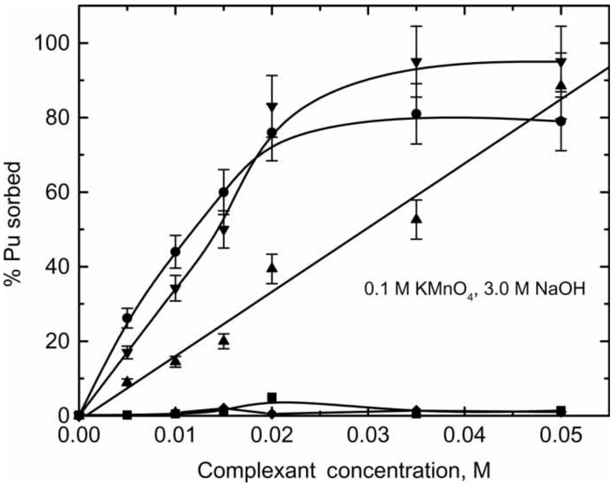

Figure 5. Percentage of plutonium sorbed onto MnO_2 created as a result of the oxidation of solutions of organic complexants by alkaline permanganate: (▼) gluconate, (▲) glycolate, (●) edta, (■) citrate, (◆) oxalate.

Since oxalate is apparently not oxidized in alkaline permanganate solutions, it could be proposed as an end product for the oxidation of the larger species (citrate is excluded because we see no evidence for its oxidation under these conditions)

$$\text{glycolate: } C_2H_3O_3^- + 5OH^- \rightarrow C_2O_4^= + 4H_2O + 4e^- \quad (6)$$

$$\text{gluconate: } C_6H_{11}O_7^- + 21OH^- \rightarrow 3C_2O_4^= + 16H_2O + 16e^- \quad (7)$$

$$\text{edta: } C_{10}H_{12}N_2O_8^{4-} + 30OH^- \rightarrow 5C_2O_4^= + 18H_2O + 2NH_3 + 24e^- \quad (8)$$

If permanganate is taken as the principal oxidant and MnO_2 the product of its reduction, the following reactions are postulated as the predominant thermodynamically relevant reactions:

$$\text{glycolate: } 4MnO_4^- + 3C_2H_3O_3^- \rightarrow 3C_2O_4^= + OH^- + 4MnO_2 + 4H_2O \quad (9)$$

or

$$2MnO_4^- + C_2H_3O_3^- + OH^- \rightarrow 2CO_3^= + 2H_2O + 2MnO_2 \quad (10)$$

$$\text{gluconate: } 16MnO_4^- + 3C_6H_{11}O_7^- \rightarrow 9C_2O_4^= + OH^- + 16MnO_2 + 16H_2O \quad (11)$$

$$\text{edta: } C_{10}H_{12}N_2O_8^{4-} + 8MnO_4^- \rightarrow 5C_2O_4^= + 2OH^- + 2NH_3 + 8MnO_2 \quad (12)$$

or if edta decomposes to produce three equivalents of oxalate and two of glycinate,

$$\text{edta: } 3C_{10}H_{12}N_2O_8^{4-} + 16MnO_4^- \rightarrow 9C_2O_4^= + 4OH^- + 6C_2H_4NO_2^- + 16MnO_2 + 4H_2O \quad (13)$$

Most of these reactions are hindered by increasing base concentration, and produce varying amounts of MnO_2 as a byproduct of the oxidation reaction. The Mn(VII):substrate equivalencies for these respective reactions are 1.33:1, 2:1 5.33:1, 8:1, and 5.33:1. Based on which species are and are not oxidized by Mn(VII/VI), it appears that secondary alcohols and amines may be susceptible to such oxidation, while carboxylate and tertiary alcohol functional groups are more resistant. It is reasonable to expect that the barrier to oxidation in these systems is kinetic in nature.

In each of these experiments, we were able to determine the amount of permanganate consumed spectrophotometrically. Assuming that the thermodynamically favored MnO_2 is the sole manganese species produced as a byproduct, the amount of MnO_2 produced in each sample can be calculated from the difference of the initial and final concentration of permanganate. The percentage of plutonium sorbed from the solution phase correlated directly with the amount of MnO_2 produced by oxidation of the organic. The correction for self-conversion of permanganate into manganate in alkaline medium was implemented by the use in calculations using the absorbance at 572 nm (the isosbestic point for both forms). The estimated stoichiometry of the $KMnO_4$ reduction reaction was equal to 5:1 for EDTA and gluconate, and 2:1 for glycolate. Assuming that Mn(VII) is the principal oxidant, these results imply the complete mineralization of glycolate to CO_2, gluconate oxidation principally to oxalate, and edta conversion principally to oxalate and glycinate (reactions 10, 11, 13).

For all of the organics deployed in this study, the percentage of plutonium sorbed was correlated with the amount of MnO_2 generated in each vial. The data is plotted in Fig. 6. The linear relationship between sorption of plutonium and amount of MnO_2 was found. The dual implications of this relationship are that MnO_2 does sorb Pu from the solution phase, and that the residual organic matter does not interfere with the progress of the precipitation reaction to maintain elevated Pu concentrations in the solution phase. Furthermore, one can conclude from these observations that the application of a readily oxidizable water-soluble organic compound subsequent to oxidative leaching of tank-waste sludges could be employed to help maintain the plutonium in the sludge phase for transport to the vitrification process. It is also apparent that high concentrations of EDTA or gluconate do not interfere substantially with the ability of MnO_2 to retain Pu from alkaline solutions.

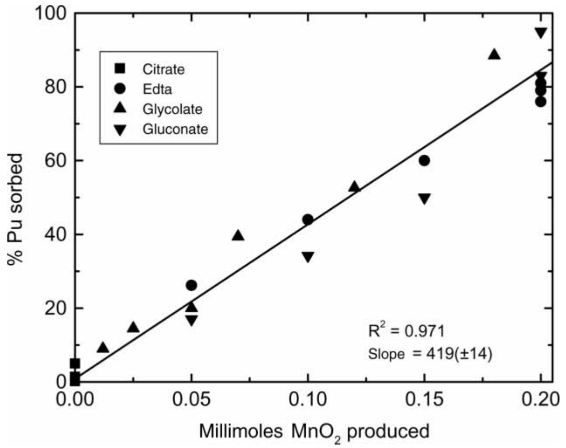

Figure 6. Plutonium sorption onto MnO_2 generated during oxidation of selected chelating agents in 3.0 M NaOH.

CONCLUSIONS

During the oxidative alkaline leaching of metals from the Hanford tank wastes two counterbalancing processes regarding plutonium chemistry must be considered. One is the possibility of co-leaching plutonium and possibly other radioactive products with the oxidized chromium. The second is redeposition of plutonium on the MnO_2 produced as a byproduct of Mn(VII) consumption. In the presence of certain organics the generation of MnO_2 can be enhanced and removal of Pu from the leaching solution can be performed with the higher efficiency. Furthermore, these results indicate that at ambient temperatures some classes of chelating agents will be resistant to oxidative degradation by alkaline permanganate. Readily oxidized organics could assist in maintaining Pu in the sludge phase after oxidative leaching. It is also apparent from these studies that the tendency for Pu to be mobilized from the sludge phase will exhibit some dependence on the composition of the sludge during oxidative alkaline leaching, responding most significantly to the stoichiometric balance between Cr(III) (or other oxidizable component) content and the amount of excess oxidant applied. It would appear that the ideal approach might well be to match the concentration of permanganate applied with the amount of oxidizable substrate present. Application of a readily oxidizable water soluble organic compound (like gluconate) might be applied to assist in maintaining Pu in the sludge phase.

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