CHARACTERIZATION OF ACTINIDES IN SIMULATED ALKALINE TANK WASTE SLUDGES AND LEACH SOLUTIONS
(Project number 81940)

Field of Scientific Research: Actinide Chemistry
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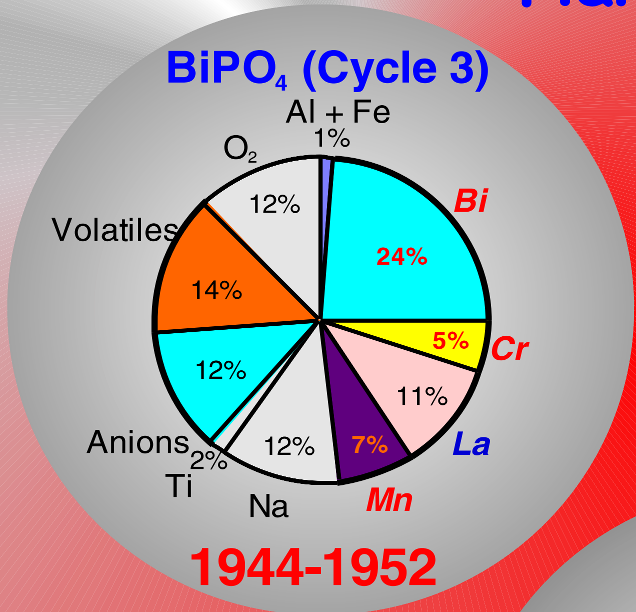
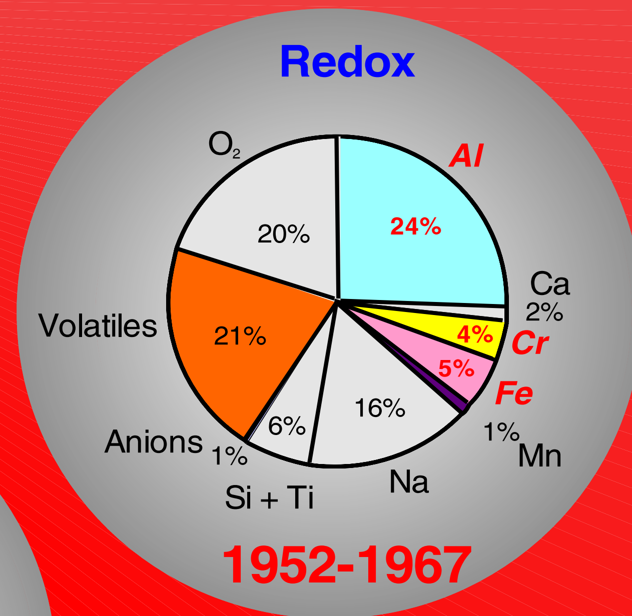
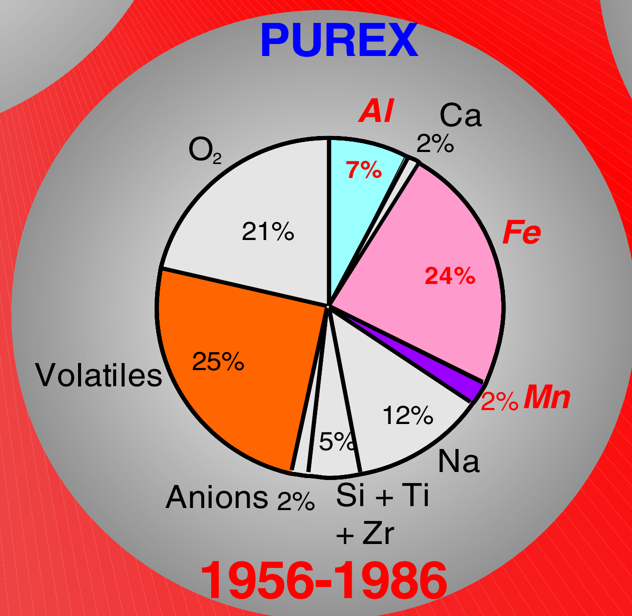
Sludge Compositions and Simulant Analyses
Hanford Waste Tanks







Volatiles represent primarily organics

O_2 represents the residue needed for mass balance

Waste Glass Limiting Species

Al: Redox>PUREX>>$BiPO_4$

Cr: $BiPO_4$>Redox>>PUREX

P: $BiPO_4$>>PUREX>Redox

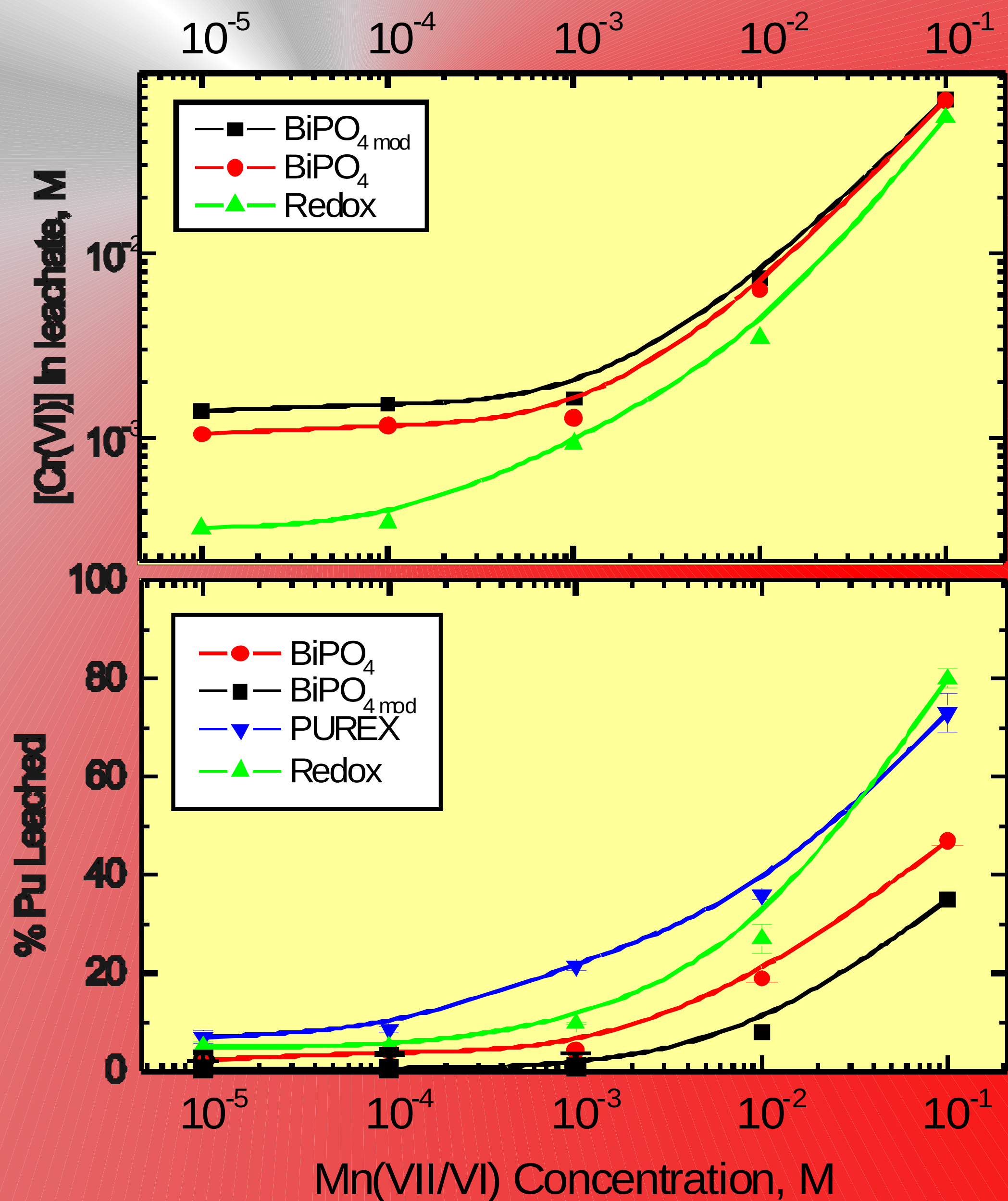
Observations and Correlations from First Stage Investigations

- Baseline sludge wash (3.0 M NaOH) results in incomplete removal of Cr, P, Al from sludge simulants - Different results for different sludge types ($BiPO_4$, Redox, PUREX)
- Cr, P, and Al removal can be increased with acid contact
- More aggressive (acids/chelating agents) treatments have varied impact on actinide mobility
- Pu and Am dissolution low in baseline sludge wash - U and Np dissolution is not negligible in baseline
- Symmetrical anionic oxy-hydroxides dominate Np speciation in 1-5 M base but...
- Chelating agents alter speciation of actinides in strong base
- Speciation of U, Np, Pu oxide/hydroxides are not identical in strong base
- Uranium species in sludge simulants are different
- Oxidative scrubs (e.g., to enhance Cr removal) likely to shift actinides to higher oxidation states

Four Tasks Pursued During Second Cycle

- **To determine the potential impact of oxidative leaching (e.g., with permanganate or ferrate) on actinide speciation.** Might it be more advantageous to employ an acid sludge wash (using reducing conditions) followed by cleanup of the actinides from the dissolvate?
- **To develop new insights into the impact of chelating agents on speciation of actinide ions in alkaline media.** Expand the previous effort to assess the impact of powerful chelating agents like edta on the solubility and speciation of reduced actinides. Investigation of the rates and mechanisms of actinide interactions of redox active sludge components and radiolysis products will also be pursued optimize contact time.
- **To determine the impact of procedures for enhancing Al dissolution from sludges on the speciation of actinide ions.** Our first stage results suggest an acidic scrub employing actinide oxidation state control (e.g., to maintain PuO_2(s) as the solubility controlling species) followed by cleanup of the minor amounts of dissolved actinides using standard separations techniques is an approach worthy of consideration.
- **To continue development of meaningful correlations of experimental results** leading to discovery of “guiding principles” and a useful descriptive model for sludge performance during sludge scrubbing.

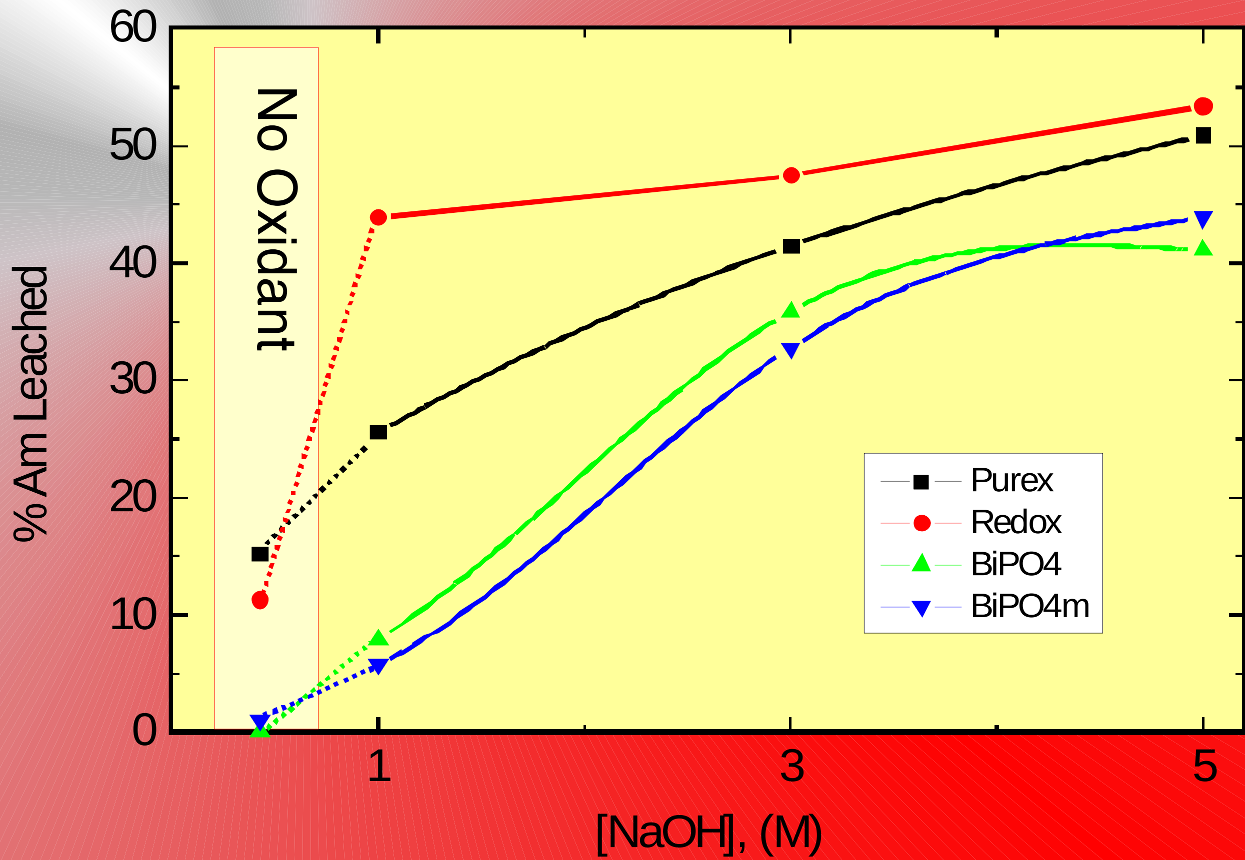
Permanganate Oxidation of Sludge Simulants



Chromium leaching from sludge simulants by permanganate in 3.0 M NaOH increased above a threshold value

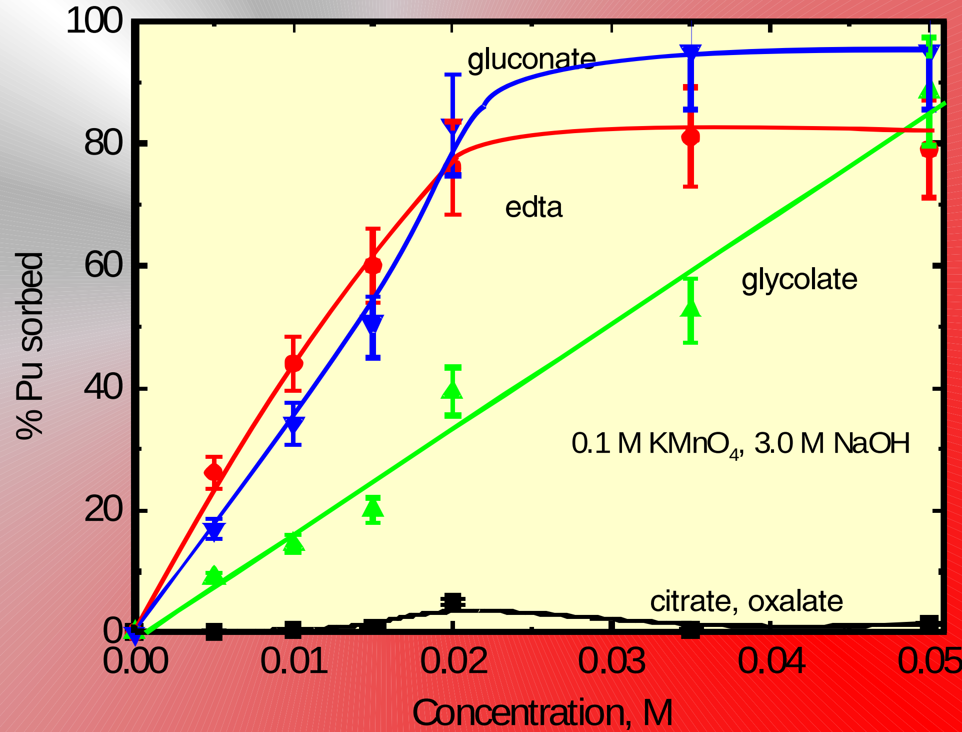
Plutonium in the supernate increases in parallel

Americium Leaching Increased in Alkaline Oxidative Treatment



- Am leach rates increase in the order $BiPO_4$ < REDOX < PUREX
- Persulfate and permanganate have similar effect on Am mobility
- Most probable Am species is Am(V)
- Am(V) not be stable indefinitely, but will persist while the oxidant is present

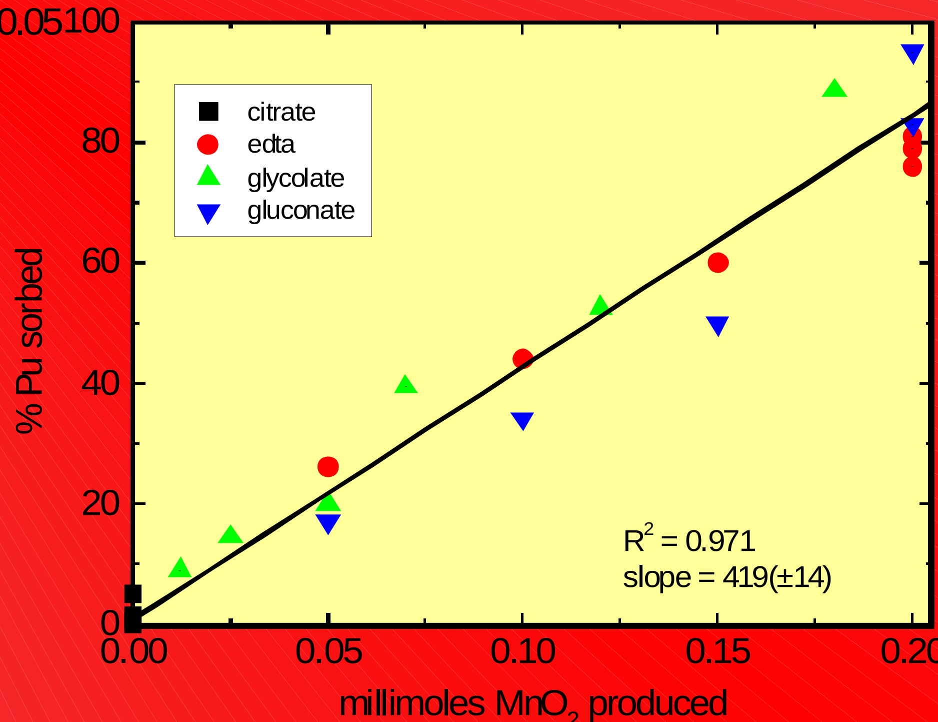
Plutonium Sorption to MnO_2 as Organics are Oxidized



Conditions of experiments:
No sludge, 60k cpm/ml ^{238}Pu

Observations:

- Plutonium sorption onto MnO_2 product correlates linearly with the amount of MnO_2 present
- edta, gluconate @ high conc does not redissolve Pu from MnO_2
- Neither citrate nor oxalate are oxidized under these conditions



Summary Oxidative Leaching

- Permanganate/manganate equally powerful oxidants
- They oxidize everything - Cr, actinides, organics, but oxalate and citrate are resistant in alkaline solutions (they do oxidize in acid)
- Product MnO_2 appears to assist with control of actinide solubility (waste glass limit for Mn is 4%)
- Different performance with respect to actinide mobilization in different sludge types, i.e., correlates with Cr content
- Caution needed to assure that the manganate/permanganate are not applied in excess of the amount required for Cr(III) oxidation
- Some readily oxidizable organics (e.g., gluconate) might be judiciously applied to control actinide solubility if excess permanganate/manganate is applied in oxidative sludge washing

New Information on Actinide Solution Species in Alkali

- $NpO_2(OH)_4^{2-/3-}$ dominant species of Np in strongly basic solutions - edta and oxalate alter this speciation
- $PuO_2(OH)_4^{2-/3-}$ species are similar, but potentials are significantly different than for Np, altering the relative stability of species
- Np(IV)/Np(V), Np(V)/Np(VI), Np(VI)/Np(VII) potentials measured in 3.0 M base
- U(VI) complexes with malonate and oxalate are significant in neutral pH, less important in concentrated base
- U(VI) complexes with HEDPA (1-hydroxyethane-1,1-diphosphonic acid) are soluble in strongly basic media - thermodynamic parameters determined
- Pu(VI) mixed hydroxycarbonate complexes identified spectrophotometrically in the pH region between stability fields of $PuO_2(CO_3)_3^{4-}$ and $PuO_2(OH)_4^{2-}$

Hanford and SRS Identified Needs - Summer 2004

Hanford Interests:

- Fundamental knowledge of waste tank chemistry
- Specific studies on the chemical behavior of oxalic acid at high ionic strength for current in-tank sluicing operations.
- Chemistry of HLW glass-limiting components Al, Cr, and SO_4^{2-}
- Further studies of the chemistry of Cr in oxidative leaching
- Supplementary treatment technologies for LAW, in particular, studies of the leaching of tank residuals

SRS Interests:

- Sodium aluminosilicate explicitly identified as a problematic species
- The tank closure program needs include improved methods for reducing the quantity of residual materials in the tanks and development of tank fill materials.

Stage 3: The Path Forward

- Continuing work on the removal of lanthanides and actinides from $Al(NO_3)_3$ by conventional solvent extraction (supports possible acid or complexometric leaching to dissolve Al)
- Chelating agents for aluminum dissolution (oxalate, gluconate, HEDPA and other phosphonates) - basic chemistry and dissolution of Al_2O_3 - extend to Fe, Cr oxides or solid solutions as time permits and interest indicates
- Actinide speciation in alkaline gluconate, oxalate, mixed oxalate - gluconate and HEDPA solutions, with and without Al present
- Aluminum leachate cleanup and control of waste glass limiting species - Precipitation/coprecipitation of heavy metal sulfates, phosphates, chromates
- Phosphate mineralization for tank backfill
- Development of guiding principles for process development - basic information for Al and actinide chemistry in alkaline media

Acknowledgments

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