

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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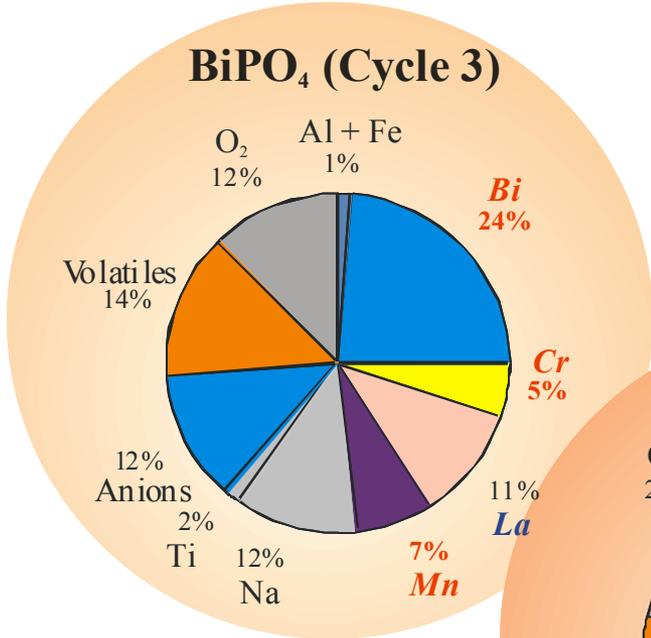
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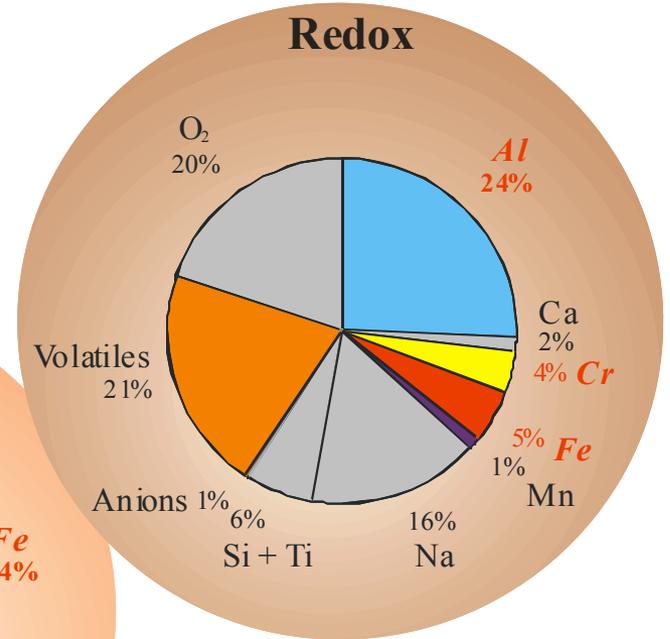
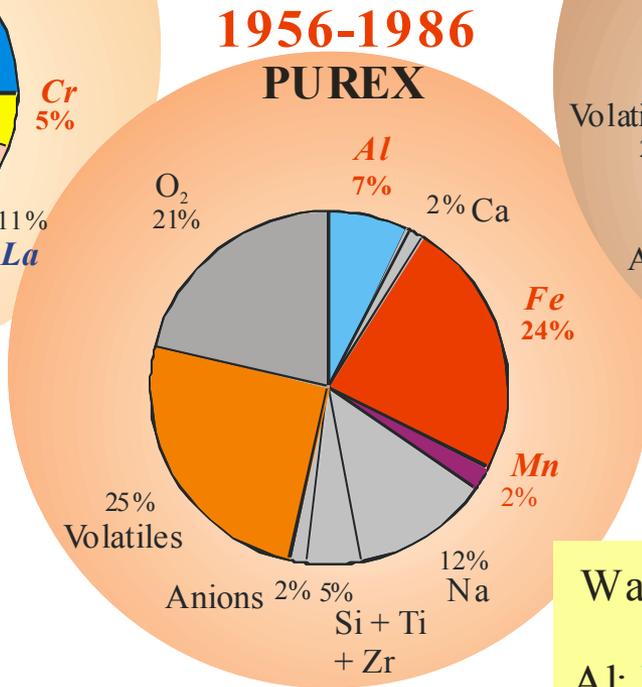
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Sludge Compositions and Simulant Analyses



1944-1952



1952-1967

Volatiles represent primarily organics

O₂ represents the residue needed for mass balance

Waste Glass Limiting Species

Al: **Redox** > **PUREX** >> **BiPO₄**
 Cr: **BiPO₄** > **Redox** >> **PUREX**
 P: **BiPO₄** >> **PUREX** > **Redox**

Observations and Correlations

Stage 1 Studies

- P Baseline sludge wash results in incomplete removal of Cr, P, Al from sludge simulants - Different results for different sludge types
- P Cr, P, and Al removal can be increased with acid contact
- P Pu and Am dissolution low in baseline sludge wash - U and Np dissolution not negligible in baseline
- P Symmetrical oxy-hydroxides dominate Np speciation in 1-5 M base - Chelating agents alter speciation of actinides in strong base
- P Speciation of U, Np, Pu oxide/hydroxides are not identical in strong base
- P Uranium species in sludge simulants are different
- P Oxidative scrubs (e.g., to enhance Cr removal) likely to shift actinides to higher oxidation states

Four Tasks Being Pursued to Extend Previous Results

- P **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 dissolve?
- P **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.
- P **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 $\text{PuO}_2(\text{s})$ 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.
- P **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.

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. They observe that:

- ! **H₂O₂** is ineffective in concentrated alkali
- ! **O₃** is rapid and effective but enhances dissolution of TRU elements and is corrosive
- ! **O₂** is effective and selective, but slow - no enhancement in dissolution of radionuclides noted - two weeks contact would be needed for practicality
- ! **Persulfate** is effective for several Cr mineral phases, but oxidizes TRU's and introduces sulfate in LAW stream
- ! **Ferrate** is rapid and effective, mobilizes little TRU, but is unstable and difficult to use
- ! **Permanganate** is rapid and effective, exhibits little TRU dissolution at low hydroxide concentration, but produces MnO₂, which can impair glass stability

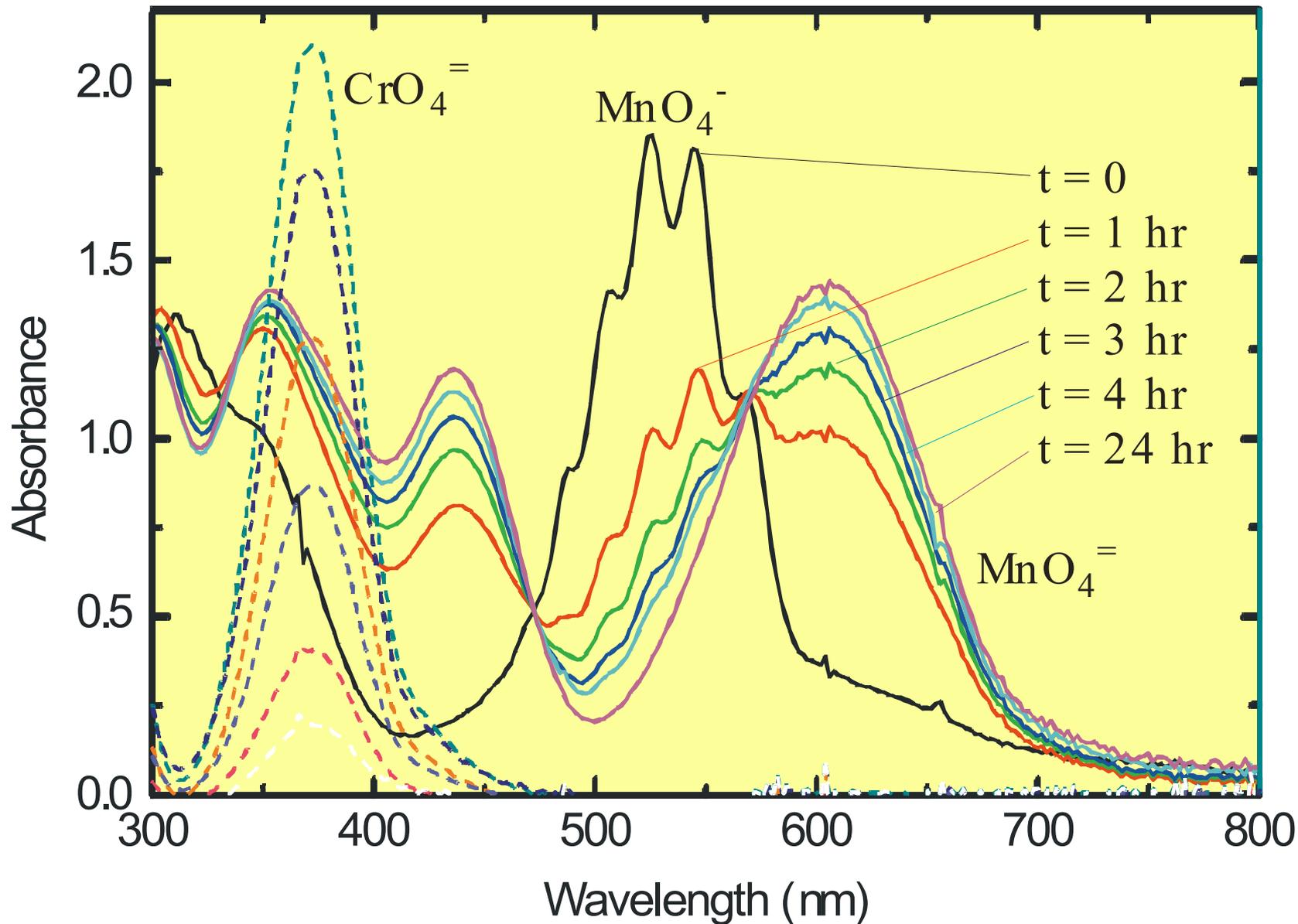
Rapko observes that with permanganate ...

- ! 1 hour contact adequate for Cr oxidation/dissolution

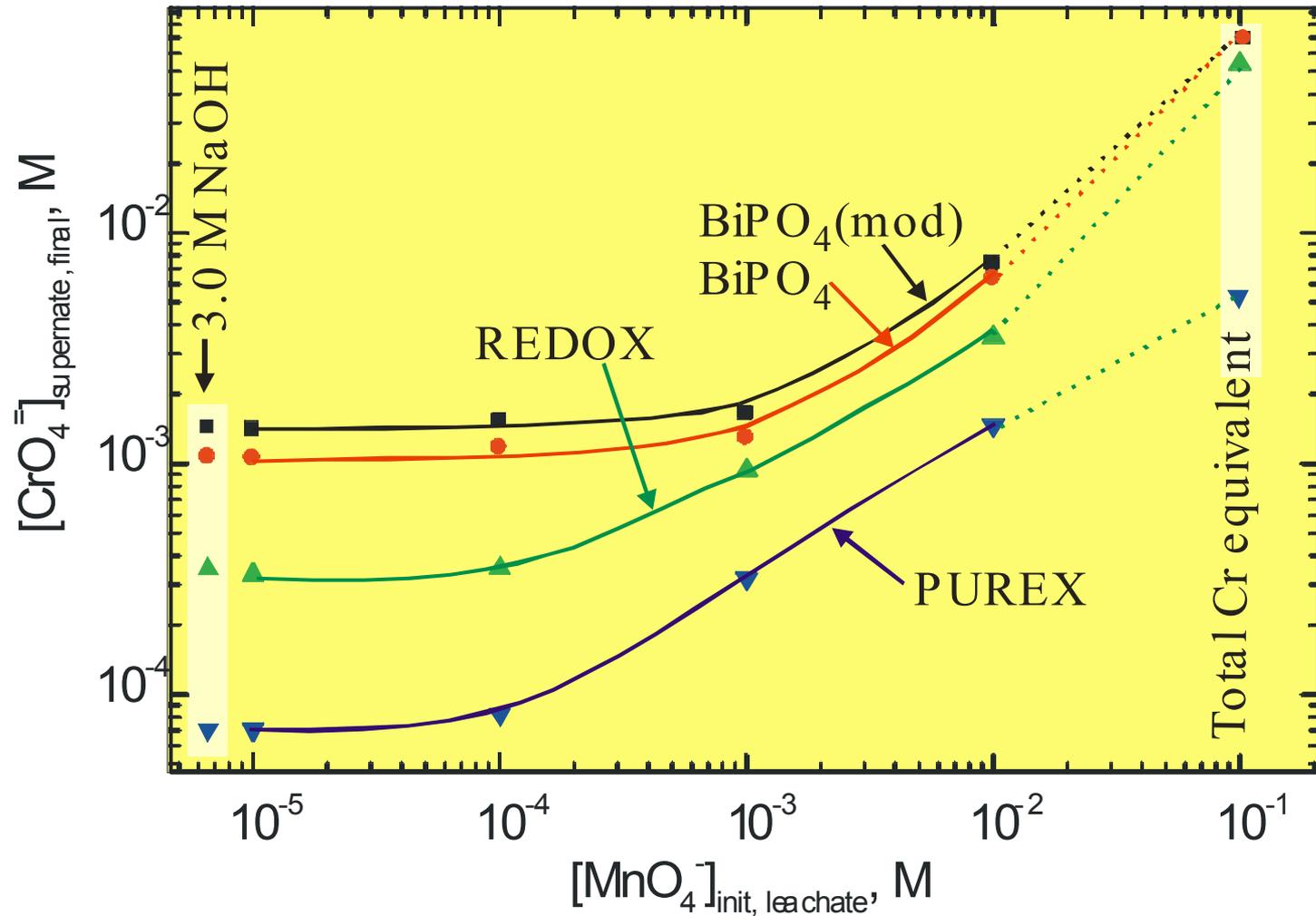
and concludes that of the several oxidants considered

- ! "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."

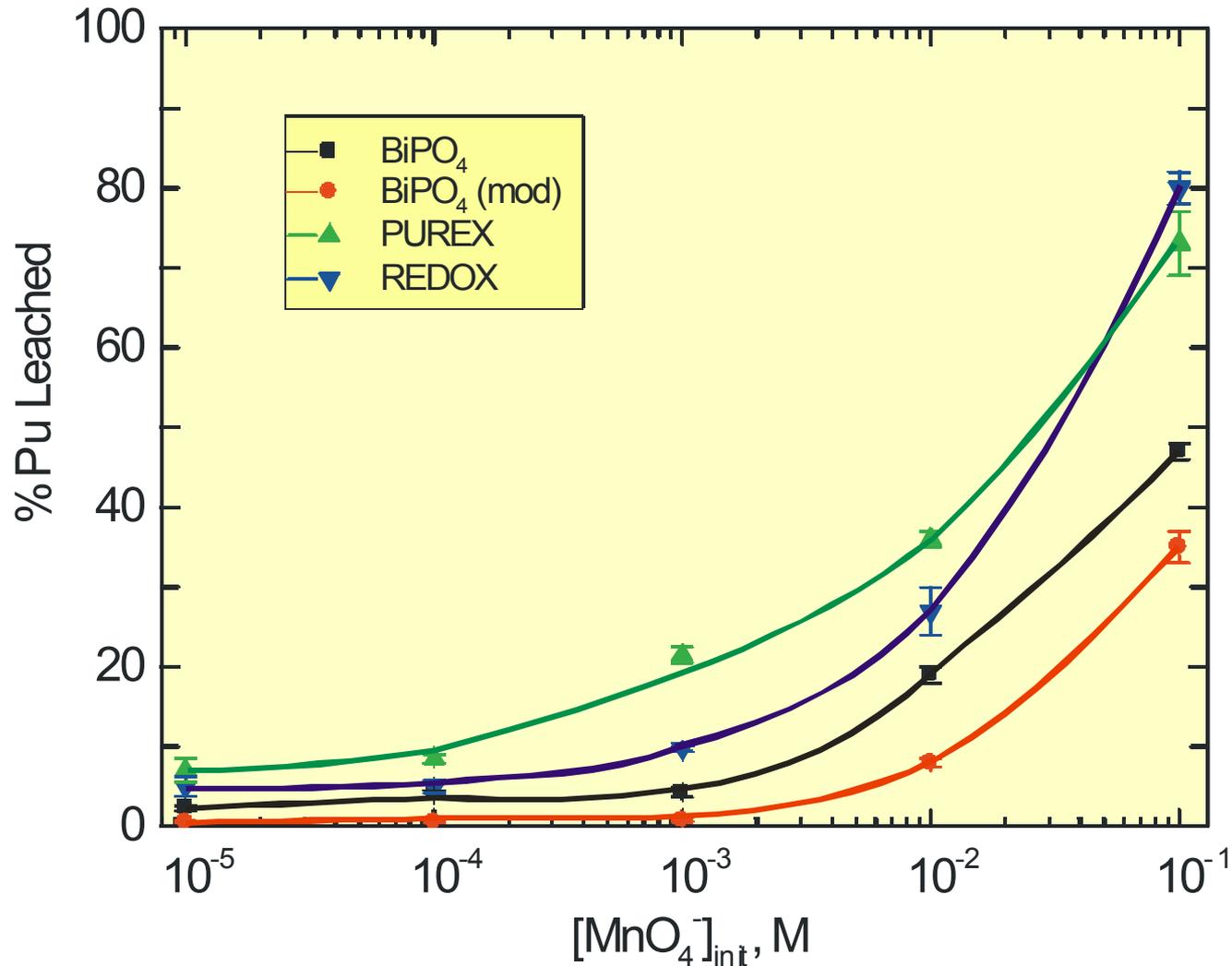
Overlap of permanganate/chromate spectra



Chromium Dissolution by Alkaline Oxidative Leaching of Sludge Simulants



Plutonium Leached from Sludge Simulants by 3.0 M NaOH/KMnO₄



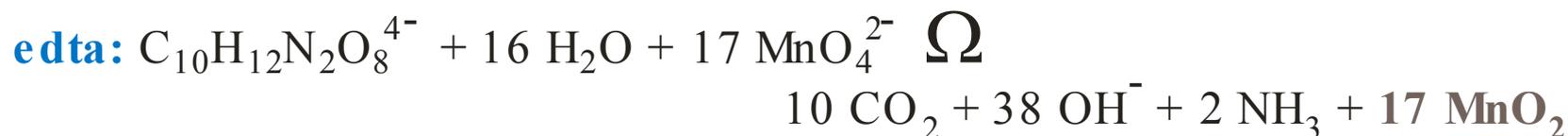
P Average of replicate samples containing oxidized and reduced Pu

P Note relative order at high $[\text{MnO}_4^-]$ with sludges is reversed relative to Cr

Complete Oxidation (mineralization) of Organics



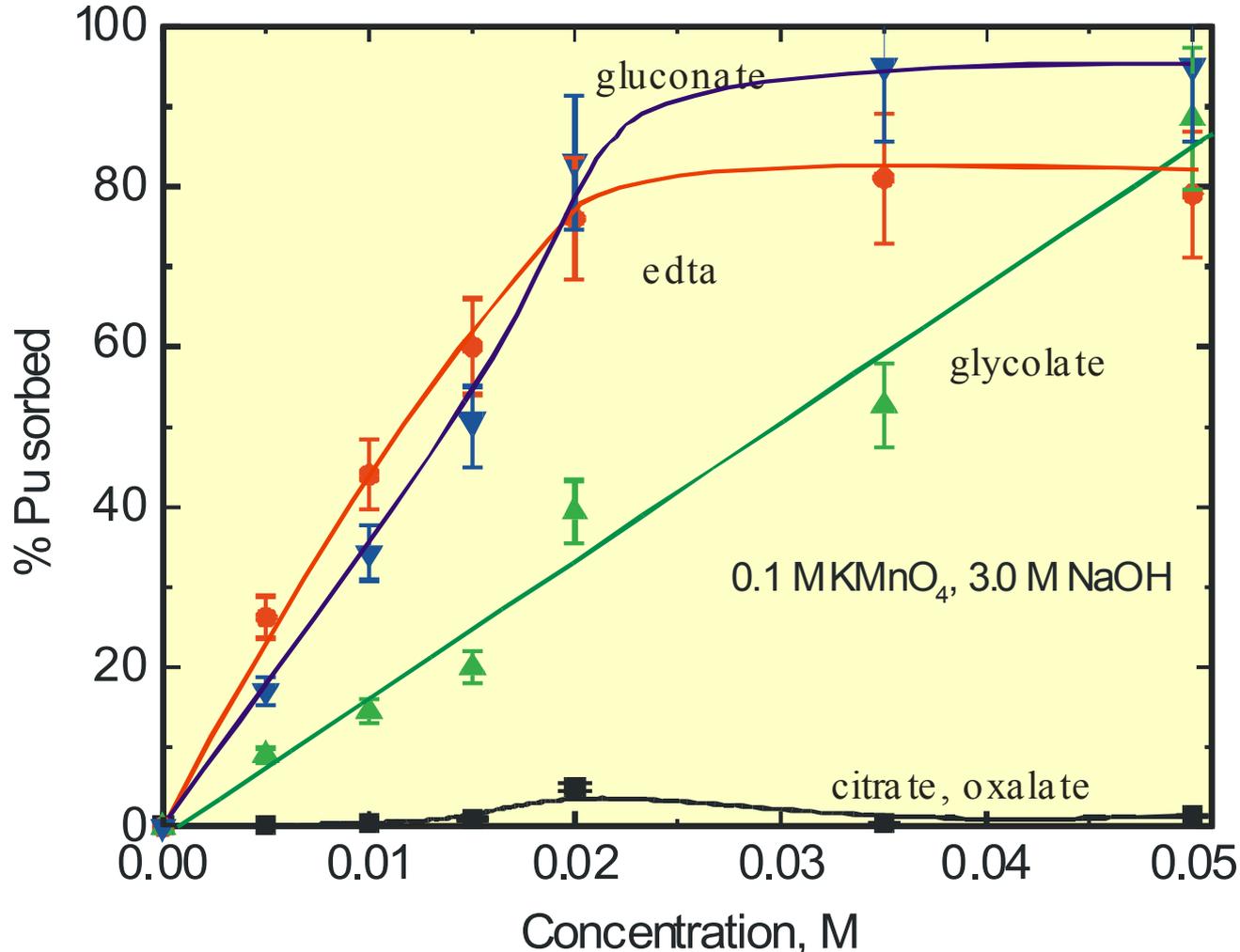
Net Reactions (Mn(VI) as oxidant):



! Oxidation reactions may produce organic intermediates resistant to complete oxidation (e.g., oxalate)

! Kinetic features can interfere with reaction progress

Plutonium Sorption to MnO_2 as Organics are Oxidized

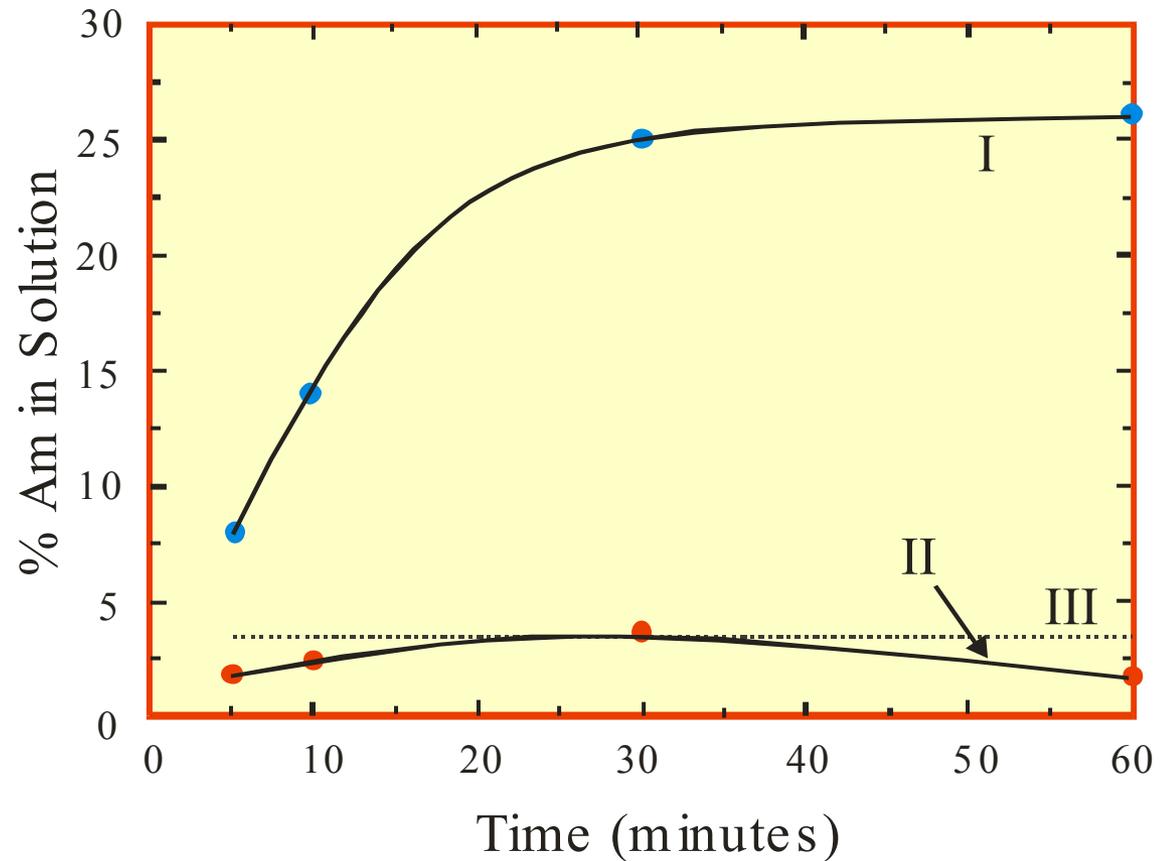


Conditions of experiments : No sludge, 60k cpm/ml ^{238}Pu

Observations :

- ! edta, gluconate @ high conc does not redissolve Pu from MnO_2
- ! Neither citrate nor oxalate are oxidized under these conditions

Oxidation of Am(III) by Persulfate in Sludge Scrub Simulant?



Total Am(init) on BiPO₄ sludge simulant: 5×10^6 Bq @ [K₂S₂O₈] = 0.2 M

- I 3 M NaOH, 100°C
- II in supernatant simulant (pH 9), 100°C
- III 3 M NaOH, 20°C

Observations Am Oxidative Leaching

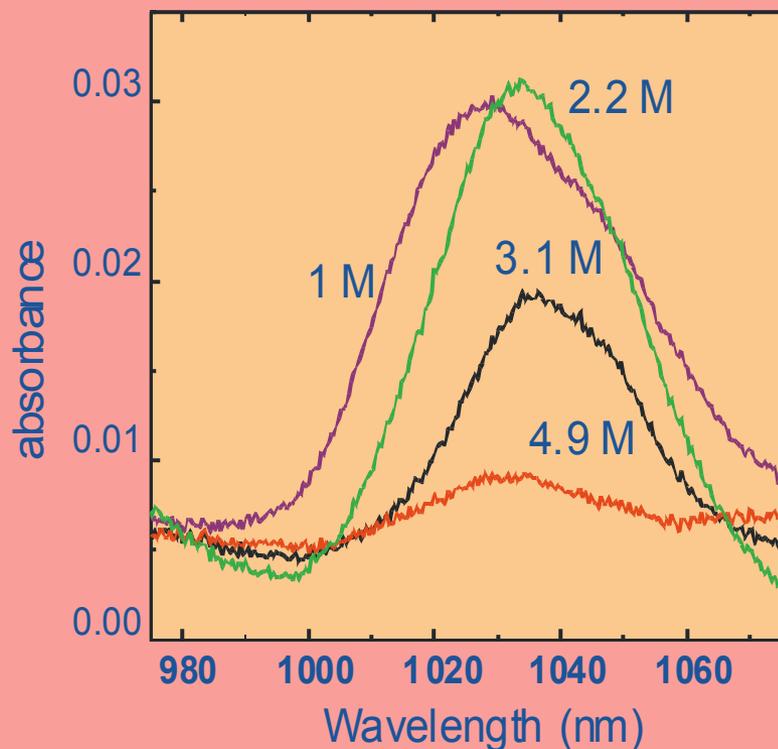
- Different sludges, different leaching patterns observed
- Effectiveness of oxidants: $\text{KMnO}_4 \sim \text{K}_2\text{S}_2\text{O}_8 \gg \text{Na}_2\text{FeO}_4$
- Increased NaOH concn (1-5 M), more Am leached from solution:
$$\text{Am}^{3+} + 4\text{OH}^- \rightarrow \text{AmO}_2^+ + 2\text{H}_2\text{O} + 2\text{e}^-$$
- Increasing temperature increases Am leaching

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 needed 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

Np(V) spectra in LiOH solutions soon after preparation

$[\text{Np(V)}]_0 = 1.12 \times 10^{-3} \text{ M}$

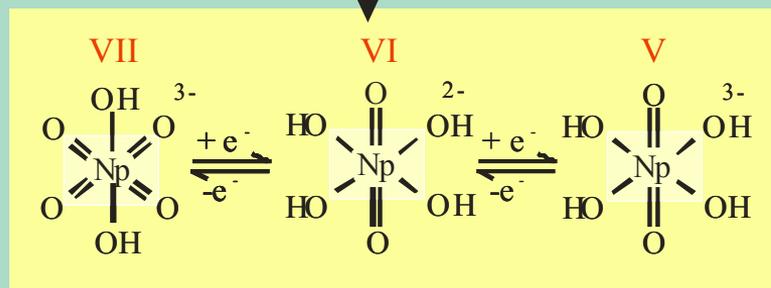


Concentrations of Np(V) in LiOH after 3 days

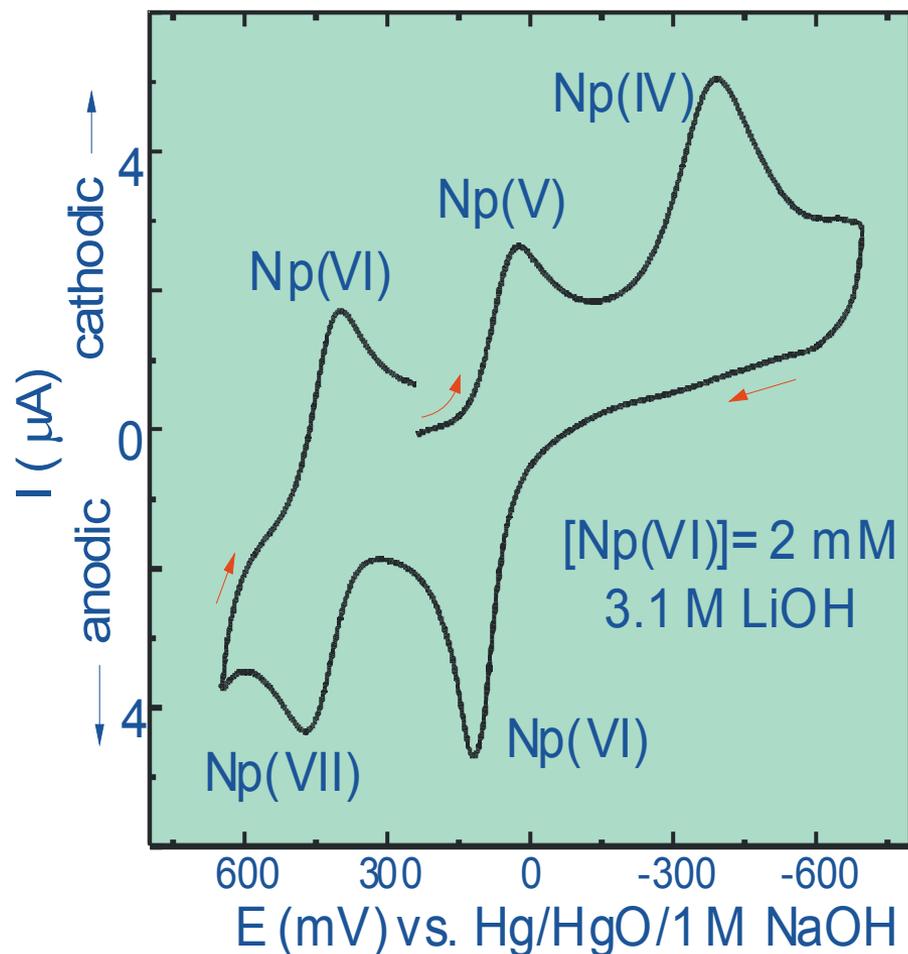
$[\text{Np(V)}]_0 = 1.12 \times 10^{-3} \text{ M}$

[LiOH], M	[Np(V)], $\times 10^{-3} \text{ M}$	$([\text{Np}]/[\text{Np}]_0)$ $\times 100\%$
1.0	0.02	1.8
2.2	0.15	13.4
3.1	0.32	28.6
4.9	1.10	98.2

No intense bands in any of the solutions after 3 days



Cyclic voltammogram of Np(VI) in 3.1 M LiOH on the Pt electrode, first scan. Scan rate 20 mV/s



Electrochemical reversibility becomes less common as the carbonate concentration increases

Np(V)-Np(VI) couples quasi-reversible in basic 1 M NaOH sodium oxalate solutions (**thermodynamic data in the literature do not explain this observation**)

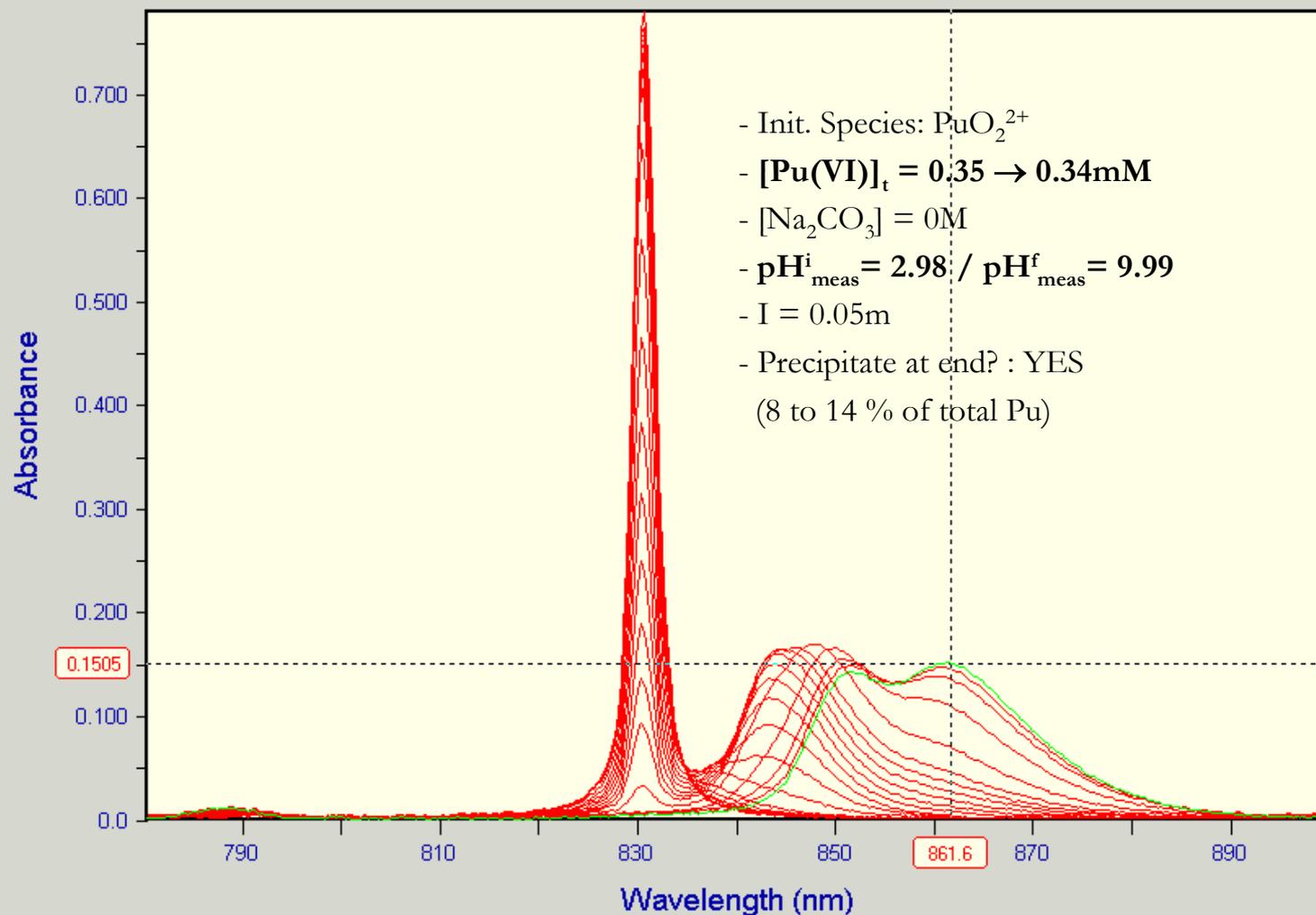
More complex speciation indicated in EDTA containing basic solutions (**thermodynamic data in the literature do not explain this observations**)

Pu(VI) in alkaline media:

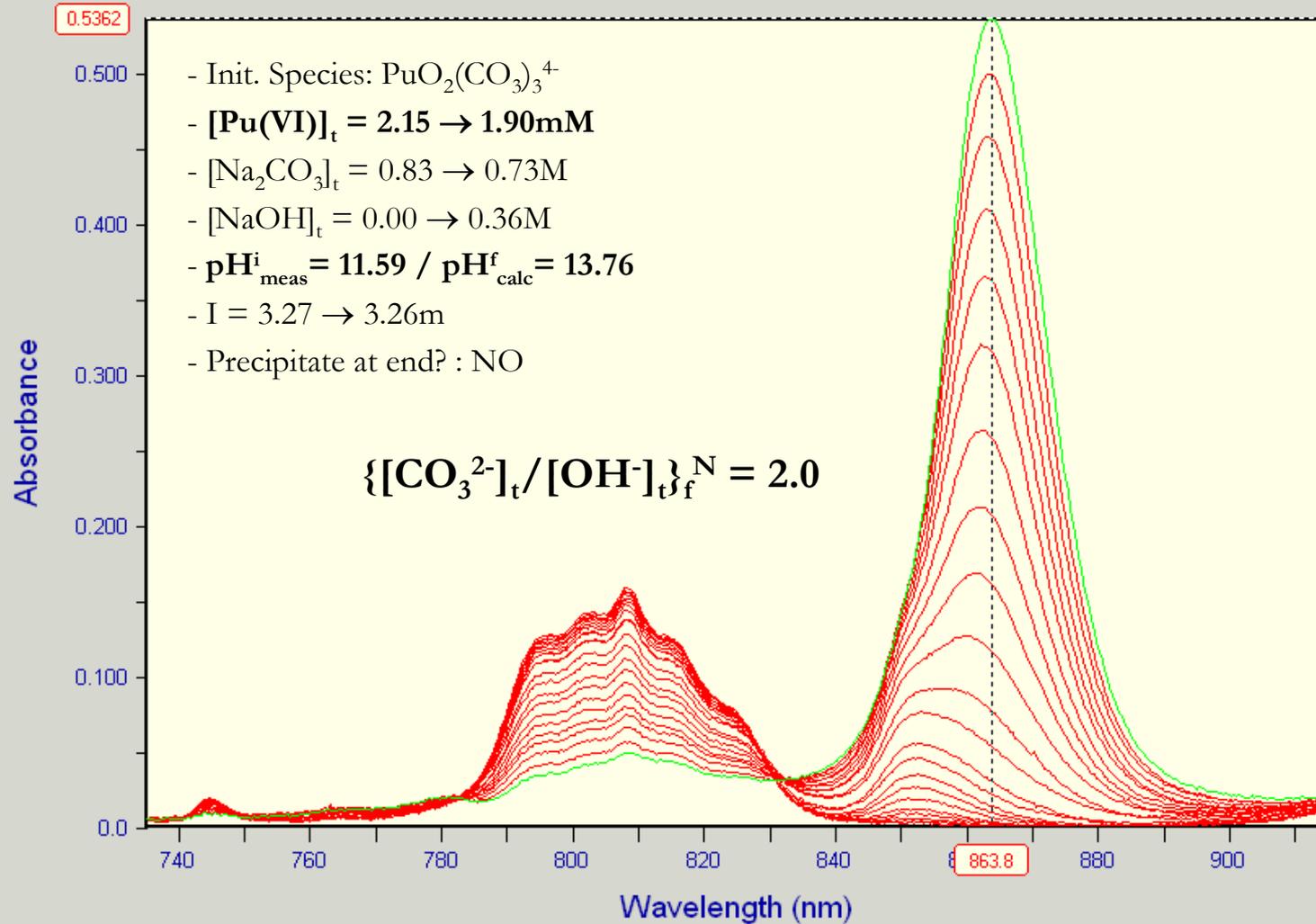
- Study motivated by the treatment of the alkaline radioactive wastes at the Hanford Site.
- Identification of Pu(VI) species in alkaline media is not straightforward and literature still presents some discrepancies among the data.
- Species accepted in the OECD database^[1]:
 $\text{PuO}_2\text{CO}_3(\text{aq})$, $\text{PuO}_2(\text{CO}_3)_2^{2-}$, $\text{PuO}_2(\text{CO}_3)_3^{4-}$,
 $(\text{PuO}_2)_3(\text{CO}_3)_6^{6-}$, $\text{PuO}_2(\text{OH})^+$, $\text{PuO}_2(\text{OH})_{2(\text{aq})}$ and
 $(\text{PuO}_2)_2(\text{OH})_2^{2+}$.

• [1] OECD-NEA, Chemical Thermodynamics of Np and Pu, Elsevier publisher, Vol. 4, 2001.

Experiment 1: $\text{PuO}_2^{2+} + \text{OH}^-$:



Experiment 5: $\text{PuO}_2^{2+} + \text{CO}_3^{2-} + \text{OH}^-$:



Results: $\log_{10}\beta^*(0)$ and associated spectral parameters

species	$\log_{10}\beta^* \pm \sigma$	Literature (OECD)	λ_{\max} (nm)	FWHM (nm)	ϵ ($M^{-1}cm^{-1}$)	Nb expts
PuO_2Cl^+	0.6 ± 0.1	0.70 ± 0.13	837.6	10	194	2
$PuO_2(OH)^+$	-5.3 ± 0.3	$-(5.5 \pm 0.5)$	843.6	10	130	2
$PuO_2(OH)_2$	-13.0 (fixed)	$-(13.2 \pm^{0.5}_{1.5})$	851.0	12	180	(fixed)
$PuO_2(OH)_3^-$	-22.4 ± 0.3	≤ -19 (Np/U)	861.6	14	140	8
$PuO_2(OH)_4^{2-}$	-36.6 ± 0.9	≤ -33 (Np/U)	Non absorbing			8
$PuO_2(CO_3)(OH)_2^{2-}$	-9.7 ± 0.3	n.a.	852.3	18	145	8
$PuO_2(CO_3)(OH)_3^{3-}$	-23.4 ± 0.7	n.a.	869.0	19	110	8
$(PuO_2)_2(OH)_2^{2+}$	-7.6 ± 0.1	$-(7.5 \pm^{0.5}_{1.5})$	848.7	15	240	2



Give best results with Specfit/32



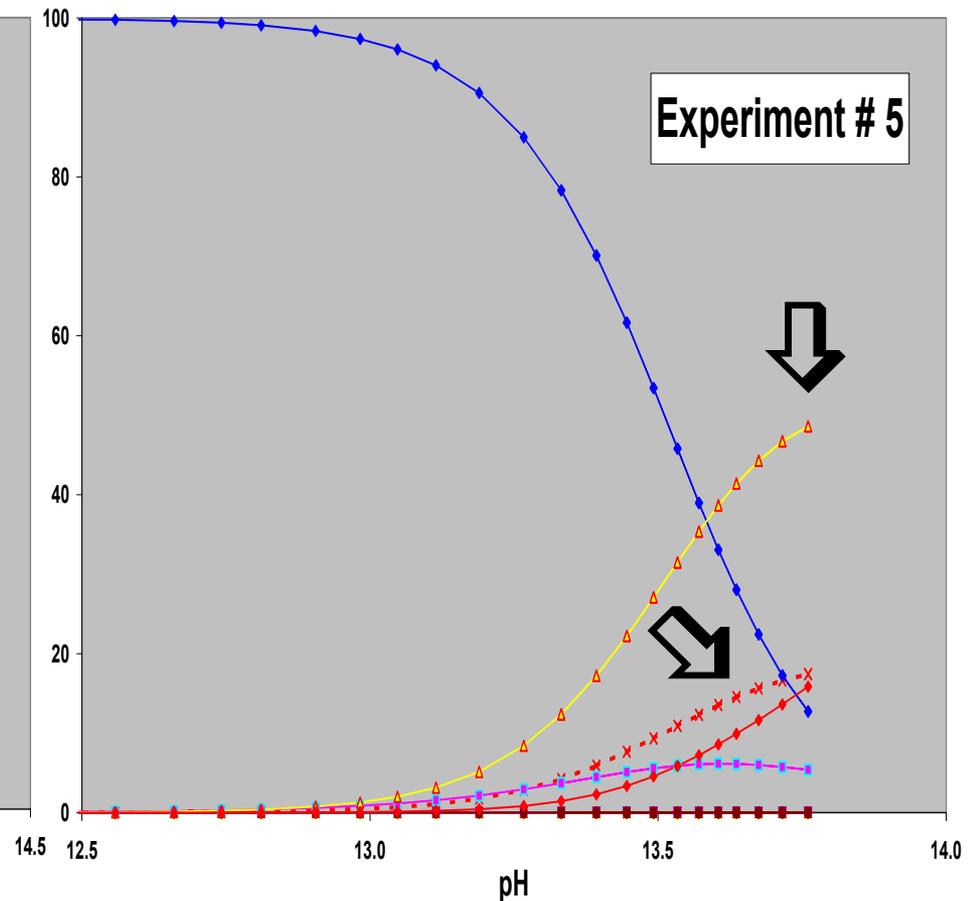
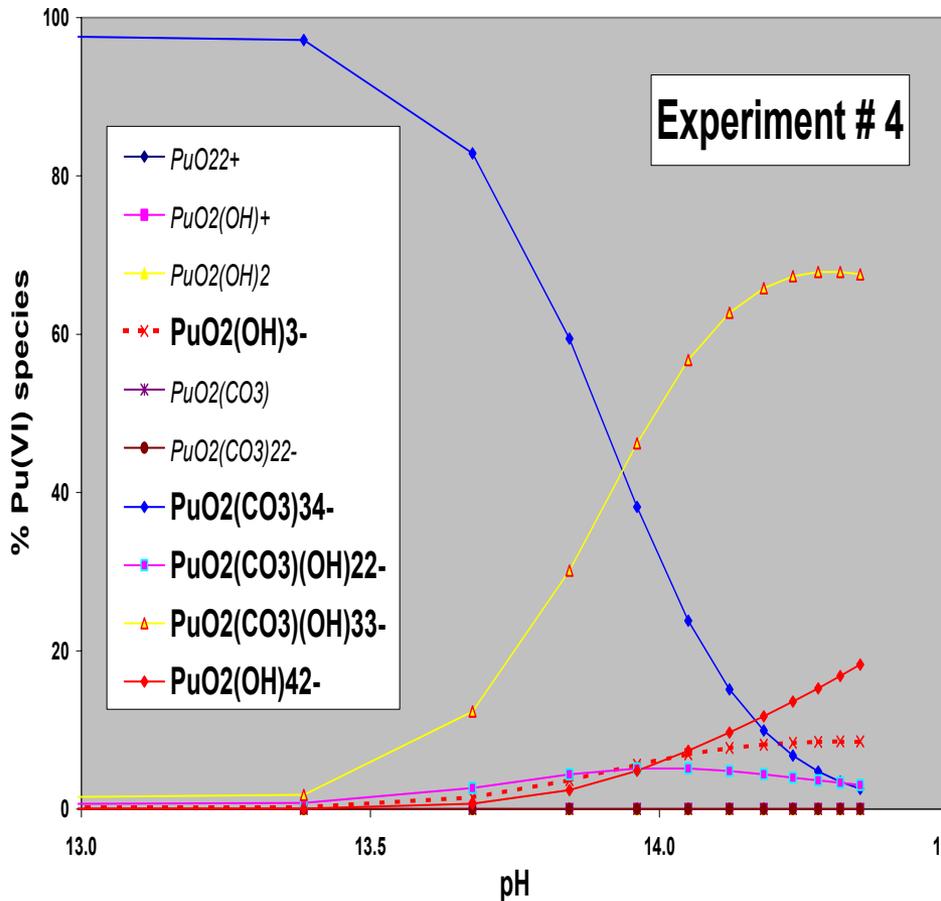
What about polymeric species ?

Pu(VI) speciation (2)

Effect of: I(m) or MINOR polynuclear species (hydroxide and/or carbonate and/or metastable) ...?

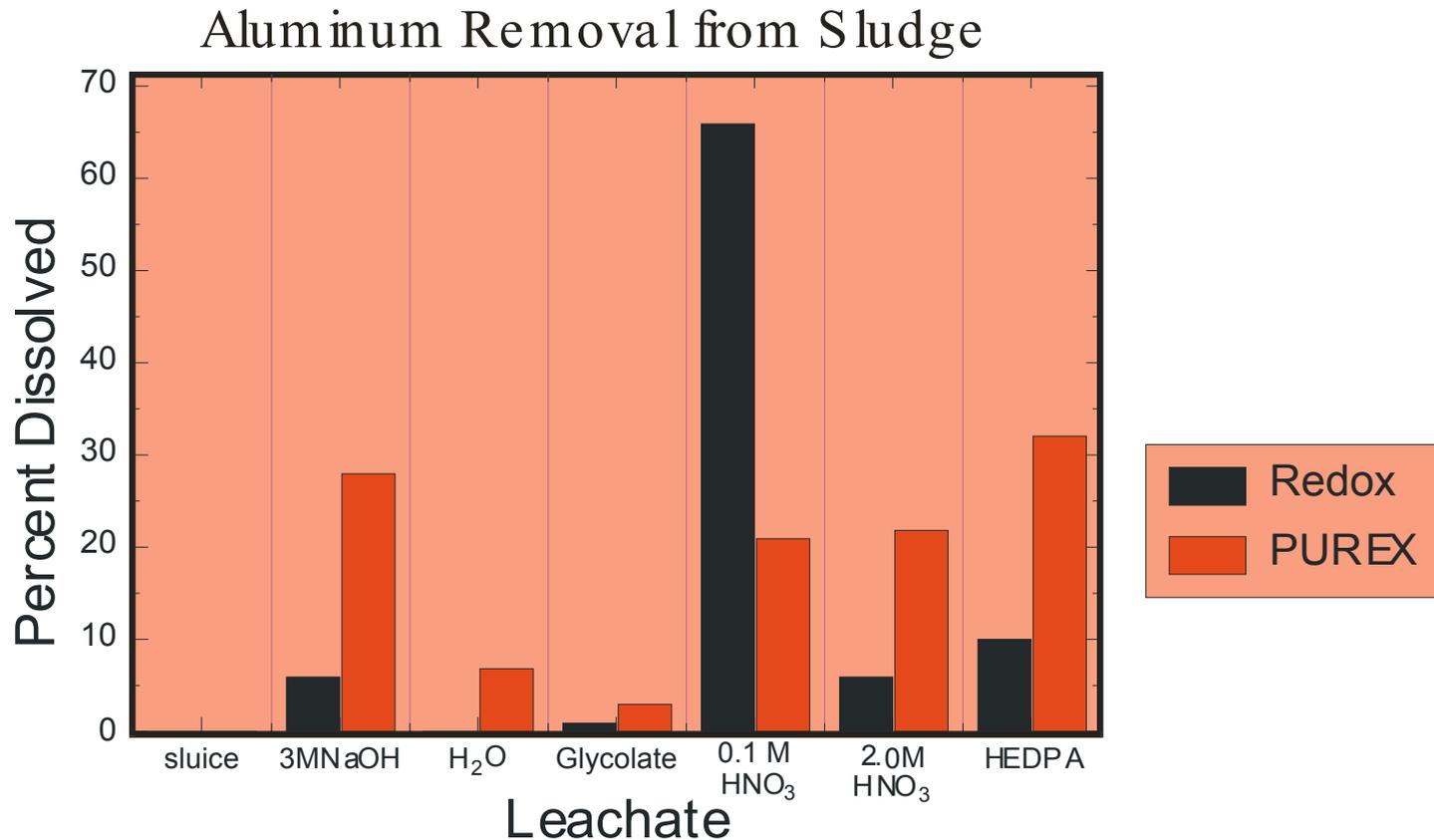
$$\{[\text{CO}_3^{2-}]_t/[\text{OH}^-]_t\}_f^N = 1.6$$

$$\{[\text{CO}_3^{2-}]_t/[\text{OH}^-]_t\}_f^N = 2.0$$



Sludge Washing Observations III (What about Al and P?)

From BiPO_4 sludge simulant, about 10 % of P (each) is removed in 3.0 M NaOH and 2.0 M HNO_3 leaches



Complexation of U(VI) with HEDPA in acidic and basic media

- Potentiometry used to obtain formation constants:
 - U(VI):HEDPA (M:L ratio 1:1, 1:2, 1:4) titrations
 - Focus on complexes in alkaline solutions
- Calorimetry used to obtain enthalpy and entropy of complexation
- Spectroscopic techniques (*e.g.* EXAFS, P-31 NMR) used to obtain structural information

Four Tasks Being Pursued to Extend Previous Results

- P **To determine the potential impact of oxidative leaching (e.g., with permanganate) on actinide speciation.** Permanganate does oxidize Pu, Am, but MnO_2 helps control “solubility”. Oxidizable organics can assist in solubility control, but balance between permanganate consumption and actinide complexation may be delicate. Other “consumables” to consider?
- P **To develop new insights into the impact of chelating agents on speciation of actinide ions in alkaline media.** Mixed complexes are formed that could impact Pu solubility and the validity of the thermodynamic modeling. Additional studies of Pu speciation in alkaline citrate or oxalate planned
- P **To determine the impact of procedures for enhancing Al dissolution from sludges on the speciation of actinide ions.** Preliminary U-speciation work underway with chelating agent HEDPA in alkaline solutions. Separations (by SX/IX) of oxidized An from acidic $\text{Al}(\text{NO}_3)_3$ solutions (to decontaminate Al) next major thrust.
- P **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.** Rapko/Lumetta work connects these data to real world. The role of organics in oxidative scrubbing needs further exploration. How important can mixed complexes become (interfering with oxide/hydroxide solubility control)?

Acknowledgments

- ! Mark Jensen (ANL/CHM) consultation on many diverse aspects of this project
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