Research Program to Determine Redox Properties and Their Effects on Speciation and Mobility of Pu in DOE Wastes

G. R. Choppin, A. Morgenstern, D. Peterman, A. Irwin, K. Morris

Florida State University

D. Rai

Pacific Northwest National Laboratory

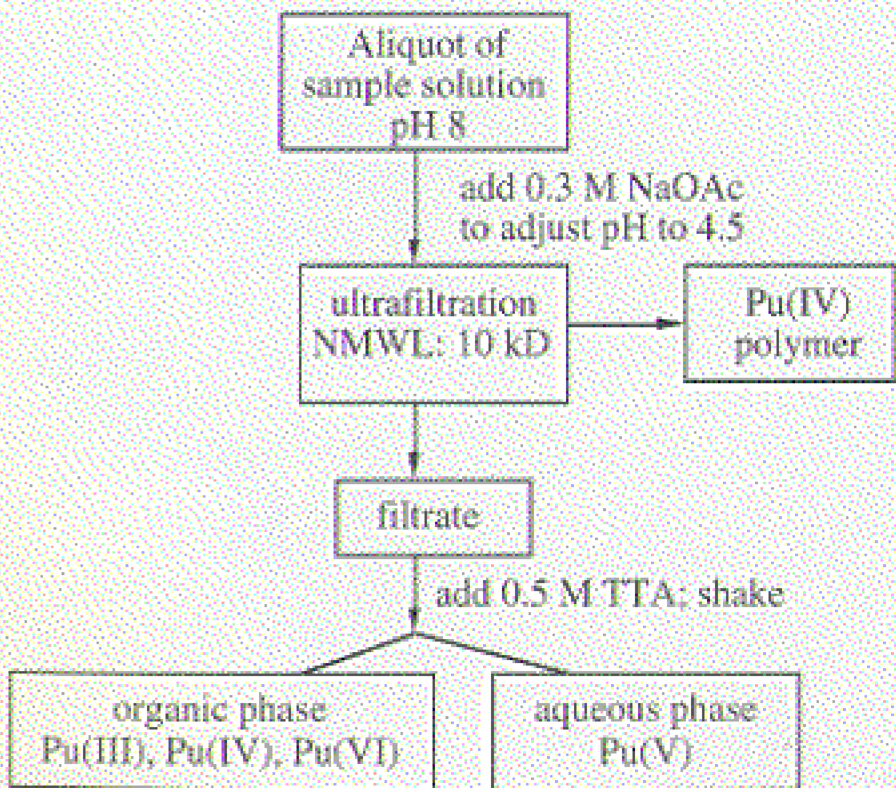
INTRODUCTION

Goal: To develop model for Pu behavior in complex chemical matrices

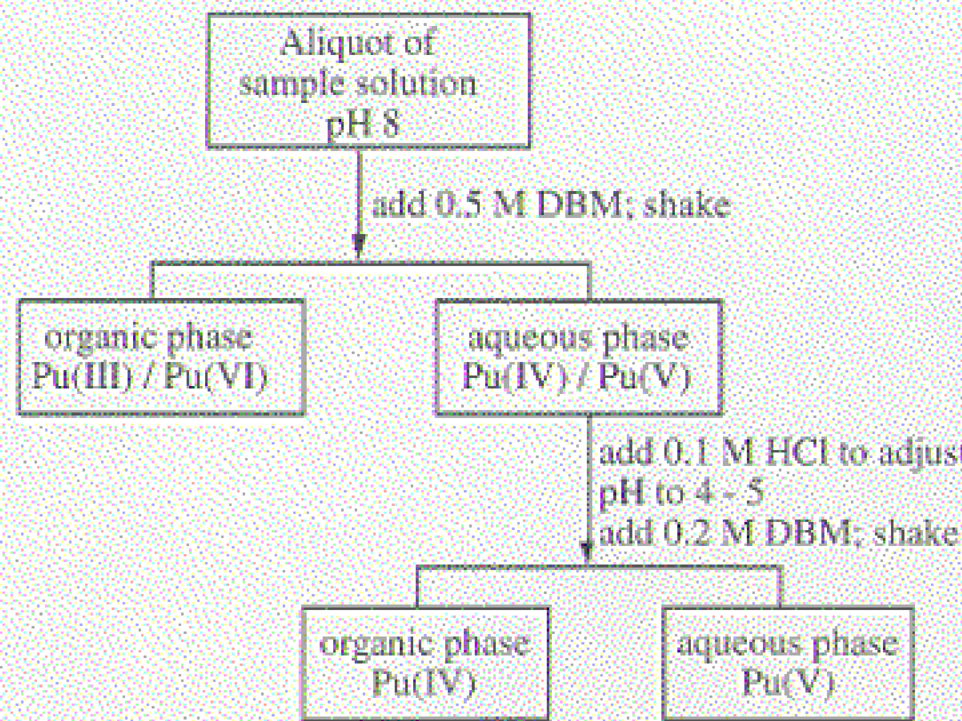
- Pu(IV), very low solubility as hydrous oxide in equilibrium with soluble PuO_2^+ over wide range of pH, E_h
- Little data on PuO_2^+ interactions with major electrolyte ions
- Need solubility data on PuO_2(am) in oxygenated and concentrated electrolytes
- Need data of complexation of Pu(IV) by strong complexants like EDTA, DTPA in wastes
- Need data on redox behavior of PuO_2^+ with NaOCl, H_2O_2 and MnO_2 in electrolyte solutions as f(pH, E_h, ionic strength)
- Develop model for Pu based on these data

Determination of oxidation state distribution

Ultrafiltration + TTA-extraction



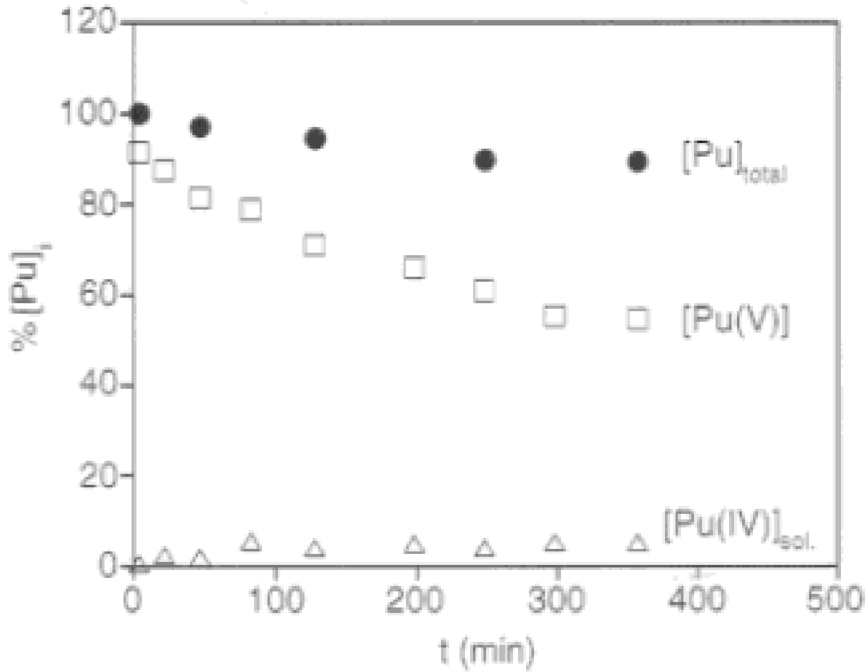
DBM-extraction



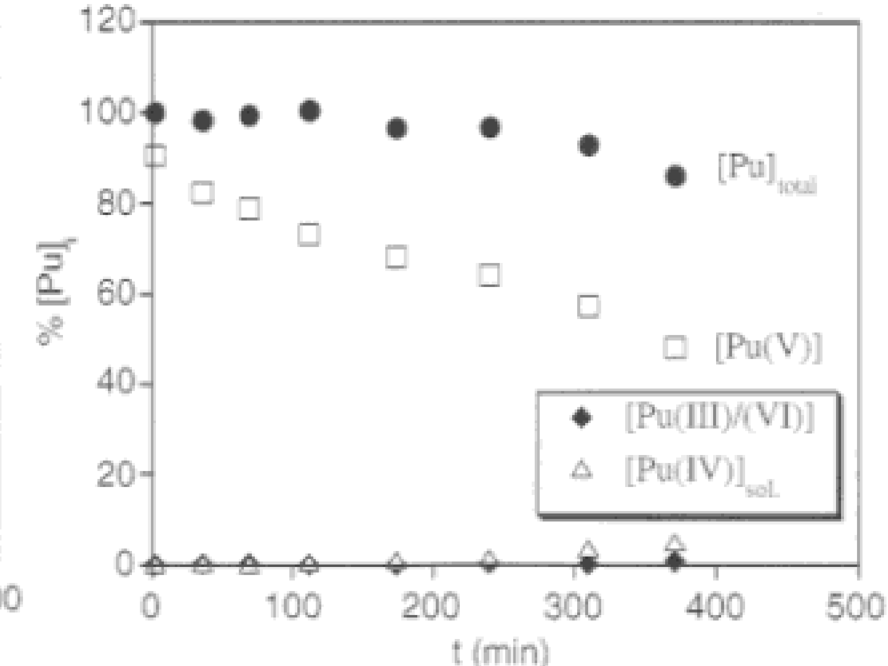
Results:
a) Ultrafiltration + TTA-extraction
b) DBM-extraction

$[H_2O_2] = 10^{-2}$ M, pH 7.9, 1.0 m NaCl, $[Pu]_t = 1.6 \times 10^{-10}$ M

a



b



Rate equation

Reduction of Pu(V) by H_2O_2
I = 1.0 m (NaCl); pH 7.9

$$-d[Pu(V)]/dt = k \cdot [Pu(V)]^n \cdot [H_2O_2]^m$$

$m = 0.94 \pm 0.14$; $n = 1$ (assumed)

$$\mathbf{k = (1.06 \pm 0.12) \times 10^9\ M^{-1}\ min^{-1}}$$

Calculated redox half lives

a) Tracer plutonium:

$[Pu(V)] = 1.4 \times 10^{-10}$ M, $[H_2O_2] = 10^{-2}$ M

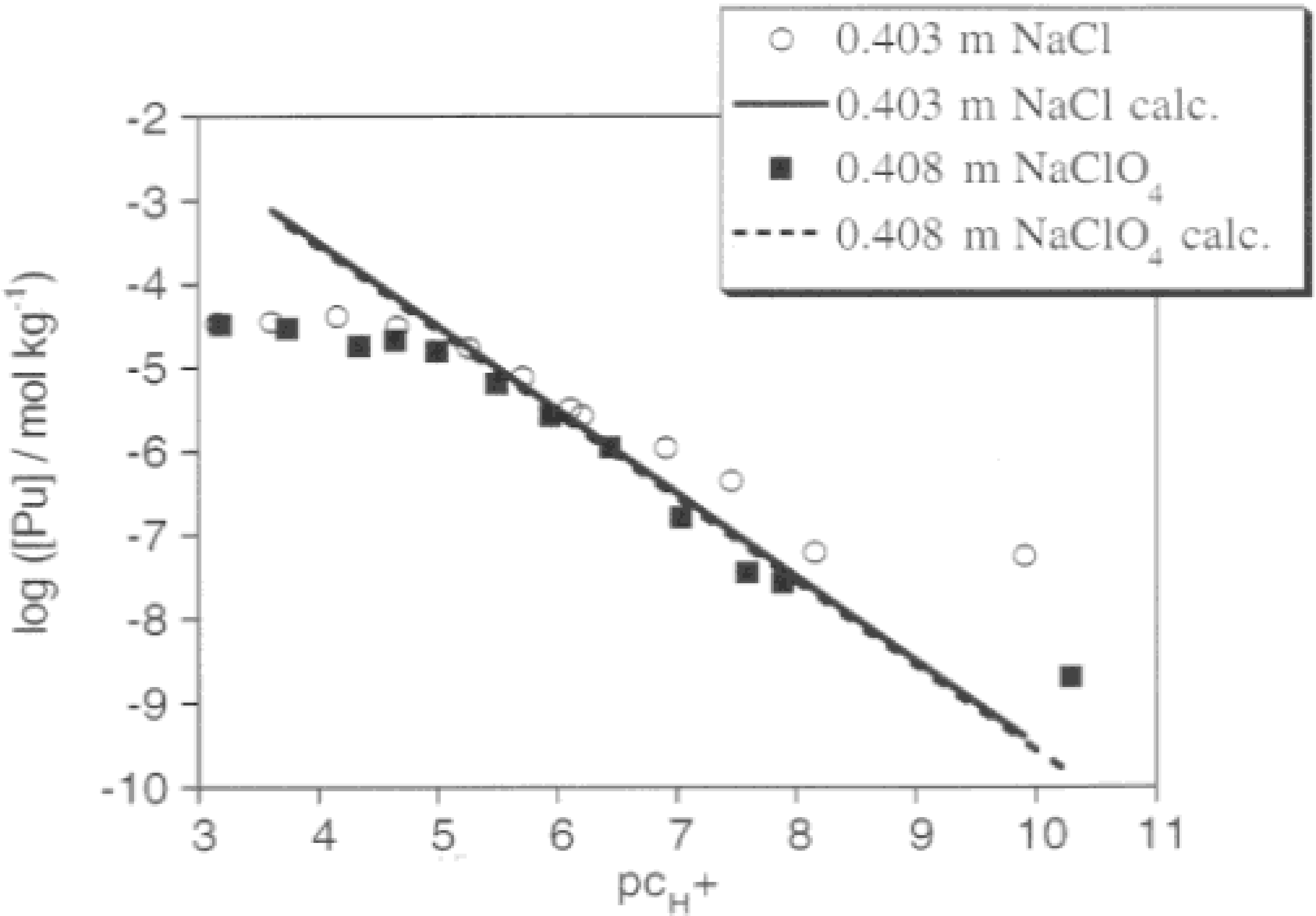
=> $t_{1/2} = 7.8$ h

b) Micromolar plutonium and H_2O_2:

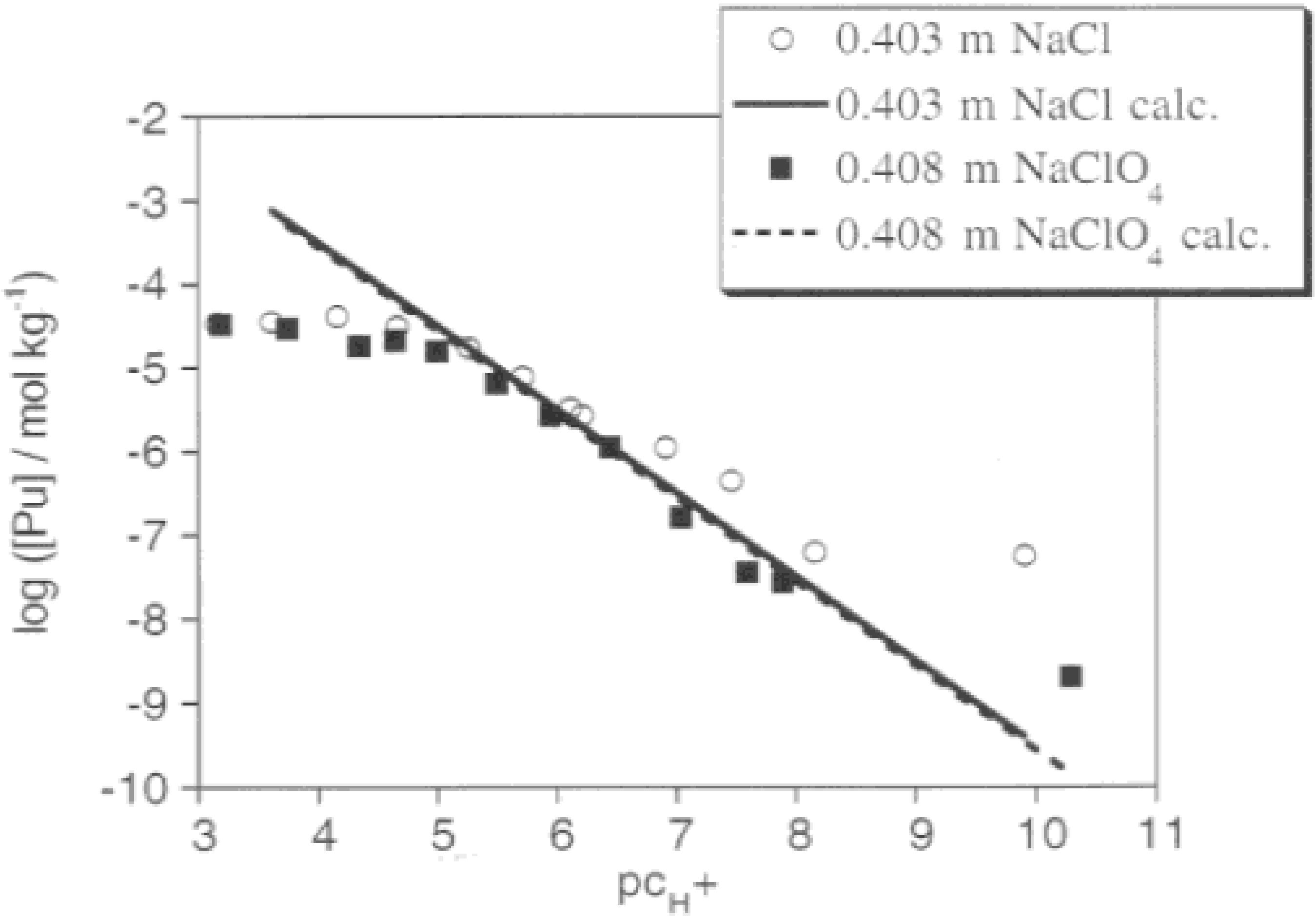
$[Pu(V)] = 10^{-6}$ M, $[H_2O_2] = 10^{-6}$ M

=> $t_{1/2} = 11$ h

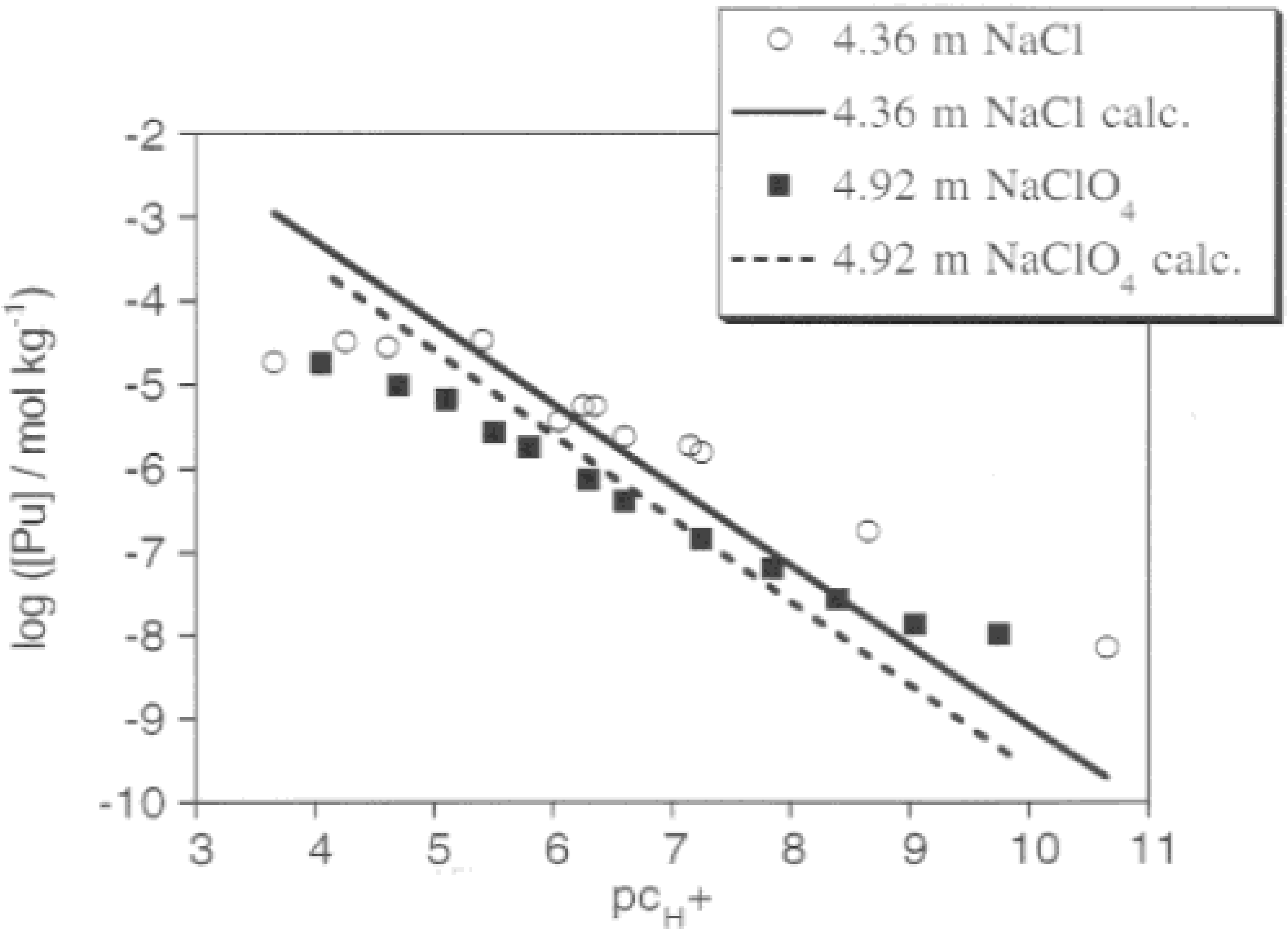
Solubility of PuO_2 (am) in 0.4 m NaCl and 0.4 m $NaClO_4$



Solubility of PuO_2 (am) in 0.4 m NaCl and 0.4 m $NaClO_4$

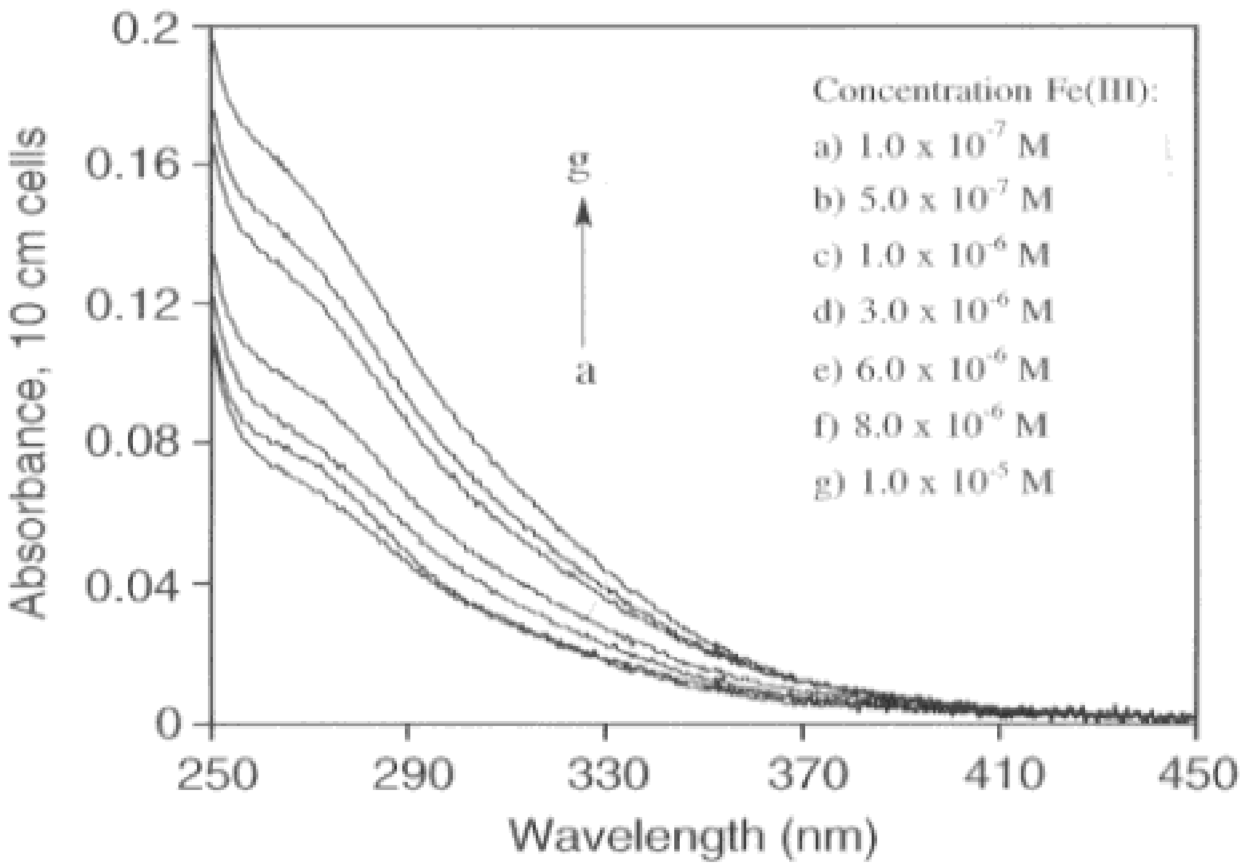


Solubility of PuO_2 (am) in 4.4 m NaCl and 4.9 m $NaClO_4$



Determination of Th(IV)-EDTA stability constants by competition with Fe(III)

$[Th(IV)] = 1.0 \times 10^{-3}$ M
$[EDTA] = 1.0 \times 10^{-3}$ M
$[Fe(III)] = 1.0 \times 10^{-7}$ M - 1.0×10^{-5} M
$I = 1.0$ M NaCl, pcH = 2.5



Determination of An(IV) + EDTA stability constants

- Pu(IV) strongly hydrolyzed -- initially investigate Th(IV) as analogue
- High An(IV)-EDTA log β ($\geq$24) values require competitive techniques for determination
- Use Fe(III) as competing metal

  $\log \beta_{[Fe(III)-EDTA]} = 23.9$ (I = 1.0)
- Add Fe(III) to Th-EDTA solution; monitor Fe-EDTA absorption spectrum

FUTURE RESEARCH

- Continue characterization of PuO_2^+ interactions with major electrolyte ions (NO_3^-, NO_2^-, etc.)
- Complete studies of PuO_2(am) as f(pH, ionic strength) in oxygenated electrolyte systems
- Continue studies of PuO_2^+ reduction kinetics by H_2O_2 and NaOCl as f(pH*, ionic strength#)
- Study oxidation kinetics of Pu(IV) by MnO_2 as f(pH*, ionic strength#)
- Complete measurement of Th(IV) and Pu(IV) stability constants with EDTA and DTPA in concentrated electrolytes
- Develop model for Pu solubility and speciation over range of pH and ionic strengths in electrolyte solutions

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* pH 6 - 10

\# ionic strengths 0.4 M and 4.0 M with NaCl and $NaClO_4$

CONCLUSIONS

- The dominant soluble oxidation state in oxygenated waters is PuO_2^+
- Ultrafiltration with TTA-extraction is effective method to monitor Pu oxidation state speciation
- H_2O_2 reduces PuO_2^+ to Pu(IV);

  rate $\propto [H_2O_2]$
- Can use Fe(III) as competitive metal ion to determine Th(IV) stability constants with EDTA,

  proceed with Pu(IV) by same method
- Pitzer ion parameters for

  $NpO_2^+ + Cl^-$, ClO_4^- apply equally well to $PuO_2^+ + Cl^-$, ClO_4^-
- The equilibrium constant for

  $PuO_2(am) + 2H_2O \Leftrightarrow Pu^{4+} + 4OH^-$ in concentrated electrolyte solutions agrees with earlier (Rai '84) values