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The analysis of Fe^{3+} and Fe^{2+} in actinide redox systems using solvent extraction

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Overview

- **Overview of WIPP**

- **Importance of Iron**

- **Optimization of experimental conditions**

- **Results**

- **Application of solvent extraction method to a real system**
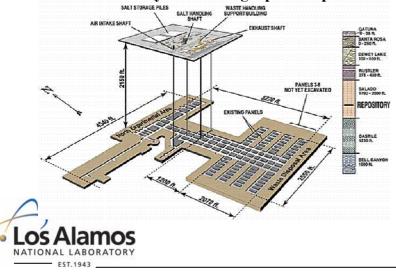
- **Further work and conclusions**

Waste Isolation Pilot Plant (WIPP) Transuranic Repository

WIPP Facility and Stratigraphic Sequence

- **WIPP initially licensed in March 1999**

- **1st recertification received in April 2006**

- **Remote-handled waste permit received in late 2006**

- **Second recertification is in progress, submittal due in March 2009**

- **Ongoing discussions of an expanded role in the Nuclear Cycle**

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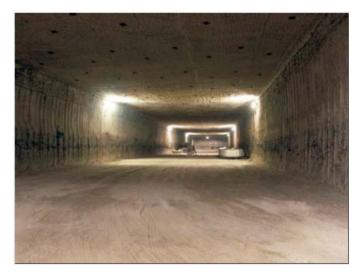NATIONAL LABORATORY
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WIPP TRU Waste Shipments

- **As of 05/30/07, 5801 shipments have been made**

- **TRU waste from Rocky Flats, Argonne, INL, PNNL, LANL, small generator sites**

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- **Excavated disposal rooms are approximately 4 m high, 10 m wide and 100 m long**

- **8 panels, with ~ 14 rooms each are currently planned (~ 3 are filled)**

- **90 348 containers emplaced**

- **Total volume is over 48000 m^3**

- **~ 90% of the Pu, by activity, is already in the repository**

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Total amount of key waste package components and actinides present in WIPP Panels 1 and 2*

Panel 1			
Radionuclides	**Amount (kg)**	**Materials**	**Amount (kg)**
Am-241	34.6	**Iron based metal alloys**	**3 327 871**
Pu	2 571	Aluminum base metal alloys	5 459
Pu-239	2 416	Other metal alloys	46 793
U	22 232	MgO	4 482 355
U-238	22 170	Cellulosics	706 141
Np-237	0.6	Plastic	522 688
Panel 2			
Radionuclides	**Amount (kg)**	**Materials**	**Amount (kg)**
Am-241	9.2	**Iron based metal alloys**	**4 922 035**
Pu	1 405	Aluminum base metal alloys	17 730
Pu-239	1 306	Other metal alloys	121 526
U	6 850	MgO	6 667 625
U-238	6 808	Cellulosics	477 213
Np-237	1.2	Plastic	876 399

*Letter from the Department of Energy, Carlsbad Field Office, to Los Alamos National Laboratory, Carlsbad Operations, dated August 28, 2006.

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Importance of iron

- **Corrosion of iron present in WIPP could generate a reducing environment**

- **Radionuclides could be maintained in lower oxidation states**
  - less soluble and thus less mobile form

- **Abiotic reduction of U(VI) to U(IV) reported in presence of iron oxides**
  - Missana *et al.* (2003) *Journal of Colloid and Interface Science,* **261,** 154-160.
  - Jeon *et al.* (2005) *Environmental Science and Technology,* **39,** 5642-5649.

- **Presence of Fe^{2+} or zero valent iron leads to reduction of Pu(VI) under brine conditions inside WIPP**
  - Reed *et al.* (2006) *Radiochimica Acta,* **94,** 591-597.

- **Abiotic reduction of Np(V) to (IV) in presence of magnetite (Fe_3O_4)**
  - Nakata *et al.* (2004) *Radiochimica Acta,* **92,** 145-149.
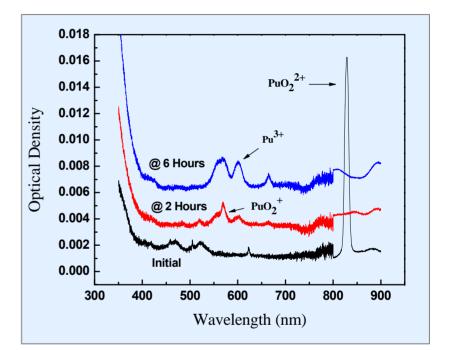
Importance of iron (continued)

- **But microbiological processes are also important**

- **Metal reducing bacteria often modulate oxidation state of aqueous iron and can reduce iron (III) phases**

- **Facultative bacteria operate in transition zone between aerobic and anaerobic conditions**

- **One example is ubiquitous *Shewanella alga***
  - Can respire on oxygen, nitrate, oxidized Mn and Fe, sulfite, thiosulfate, and higher-valent actinides
  - Couples respiration with oxidation of hydrogen or organic carbon
  - Demonstrated enzymatic reduction of U(VI), Pu(VI), Tc(VII) and Fe(III)

- **Bacteria can reduce iron making it available for the reduction of the actinides**

- **Can lead to competition between abiotic and biotic pathways**

Importance of iron (continued)

- **Reduction of Pu(VI)**
  - At pH 3 – reduction to (V) is instantaneous with slower reduction to stable Pu(III)
  - At pH 7 – reduction to (V) occurs in minutes and leads to precipitates of Pu(IV)
  - But in presence of *S. alga*, final oxidation state is Pu(III)

- **Fe^{2+} is responsible for reduction of actinides**

- **To understand mechanisms, must be able to measure both oxidation states as reaction proceeds**

Reed *et al.* (2007) Pu Futures conference 2006 (in press)

Experimental

- **All Fe^{2+} and mixed oxidation state experiments performed inside anoxic nitrogen-controlled atmosphere glovebox**

- **U(VI) in the presence of Fe(III) carried out in dedicated fumehood**

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Choice of extractant – Why HDEHP?

- **Citrate or NTA present in biological media**
  - Solubilize Fe^{3+}

- **Have relatively high stability constants with Fe^{3+}**

- **Wanted acidic media to reduce complexation**

- **HDEHP known to be acidic extractant**

Complexant	log K
Citrate	11.2
NTA	16.00

Values are for I = 0.1 M at 25ºC for [ML]/[M][L]

log K values taken from NIST database.

Effect of acid concentration

- ***HCl provides best separation for Fe^{3+} and Fe^{2+}**

- **Varied HCl concentration from 0.05 to 4 M**

- **Iron concentration**
  - 0.5 mM

*Haggag *et al.* (1977) *Journal of Radioanalytical Chemistry,* **35,** 253-267
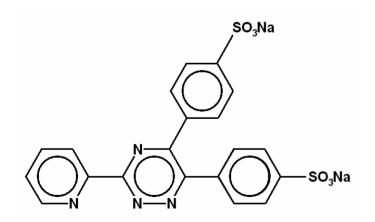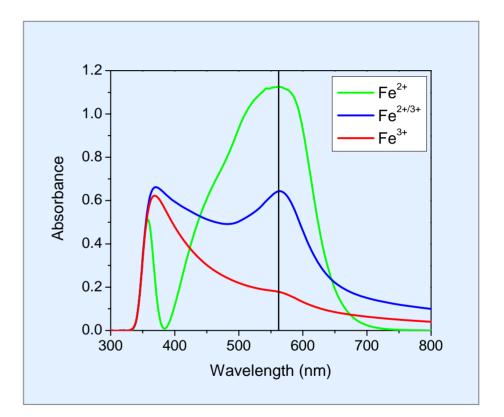
Spectrophotometry

- **Ferrozine method[1,2]**
  - Forms magenta / purple colored tris-complex with Fe^{2+} between pH 4 and 9
  - One sharp peak with maximum absorbance at 562 nm
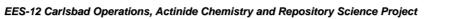
- **Fe^{2+} specific**
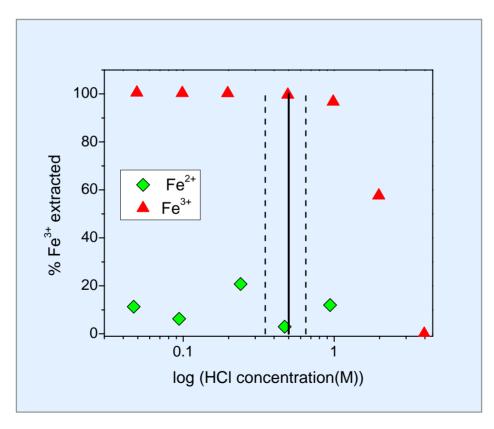 - No complex formed with Fe^{3+}

[1]Stookey *et al.* (1970) *Analytical Chemistry,* **42,** 779-781

[2]Viollier *et al.* (2000) *Applied Geochemistry,* **15,** 785-790

Acid concentration

- **0.5 M HCl best concentration for extraction**

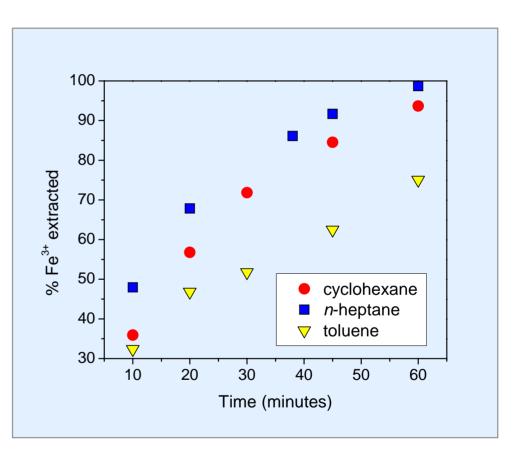- **4 M HCl best for back extraction**

Effect of diluent

- **HDEHP extracts as a dimer in solvents of low polarity[1]**

- **0.1 M HDEHP in different diluents**

- **Effect of time on extraction on Fe^{3+}**

  - Concentration = 0.4 mM

Solvent	Relative polarity[2]
cyclohexane	0.006
heptane	0.012
toluene	0.099
water	1.000

[1]Szymanowski *et al.* (1997) *Hydrometallurgy,* **44,** 163-178

[2]http://virtual.yosemite.cc.ca.us/smurov/orgsoltab.htm

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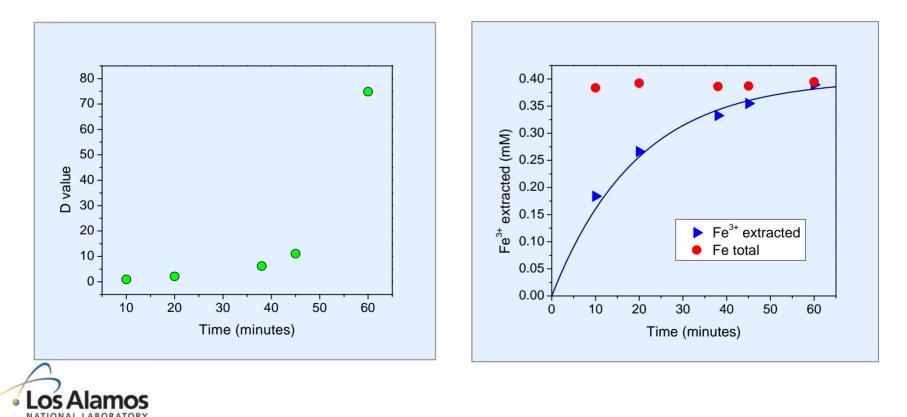NATIONAL LABORATORY
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Effect of time on HDEHP extraction

- **Rate of Fe^{3+} partitioning into organic phase is relatively slow**
  - ~ 1 hour for almost quantitative transfer (92-96%)
  - 5% min^{-1}

Solvent extraction procedure

- **Acidify sample up to 0.5 M HCl**
  - **Total Fe content**

- **Contact with equal volume of 0.1 M HDEHP in *n*-heptane for 1 hour**
  - **Fe^{2+} content from aqueous phase**

- **Contact portion of organic phase with 4 M HCl for 15 minutes**
  - **Fe^{3+} content from aqueous phase**
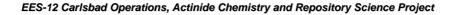
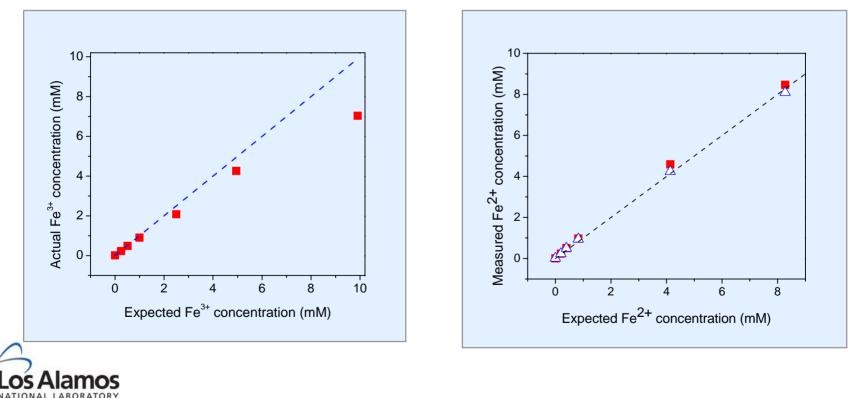- **Analysis performed with Agilent 7500ce ICP-MS**

- **Important to remove oxygen**

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Extraction capacity

- **Up to 1 mM Fe^{3+} (10% error)**

- **Up to 5 mM with ~ 15% error**

- **Up to 10 mM ~ 30% error**

- **Up to 8.3 mM Fe^{2+} over 99% will remain in aqueous phase**

Extraction mechanism for Fe^{3+}

$$M^{3+}_{(aq)} + 3(HDEHP)_{2(org)} \leftrightarrow M[H(DEHP)_2]_{3(org)} + 3H^+_{(aq)}$$

$y = -3.10312x + 1.27468$

$R^2 = 0.98283$
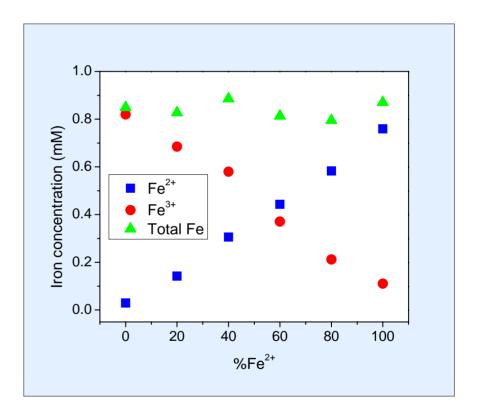
(graph: log [D] vs log [H$^+$])

- **Slope of graph = ~-3**

- **Extraction by complexation with dimer form of HDEHP molecule**

- **Suggests exchange of 3 H$^+$ for each metal cation extracted***

  - Cation exchange

$$\log D = \log K_d + 3\log[(HDEHP)_2] - 3\log[H^+]$$

Mixed oxidation state system

- **Total iron concentration = 0.5 mM**

- **Amount Fe^{3+} varied from 0 to 100%**

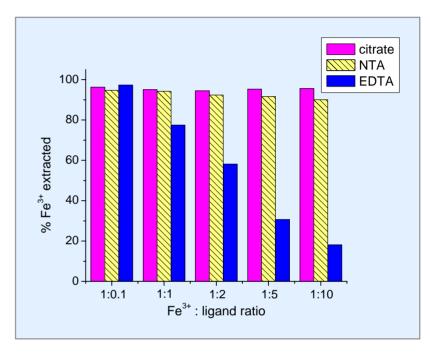- **No cross-contamination of phases from either oxidation state**

Chart legend:
- ■ Fe^{2+}
- ● Fe^{3+}
- ▲ Total Fe

x-axis: $\%Fe^{2+}$
y-axis: Iron concentration (mM)

Effect of complexant

- **Iron concentration = 0.5 mM**

- **Addition of Citrate, NTA or EDTA up to 10 times excess of Fe^{3+}**

Complexant	log K	
	Fe^{2+}	Fe^{3+}
Citrate	**4.62**	**11.2**
NTA	**8.90**	**16.00**
EDTA	**14.30**	**25.1**

Values are for I = 0.1 M at 25°C for [ML]/[M][L]

log K values taken from NIST database.
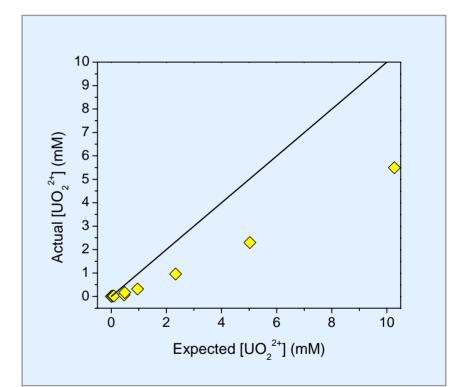

- **Little to no interference of citrate or NTA on solvent extraction method**

- **EDTA significantly affects extraction of Fe^{3+} but not Fe^{2+}**
  - Increasing HCl concentration did not correct problem

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Effect of U(VI)

- **HDEHP extracts U(VI) with the release of 2 protons**
  - Therefore U(VI) should coextract with Fe^{3+}

- **Extraction of U(VI) is fast (compared to Fe^{3+} extraction)***

- **Fe^{3+} concentration = 0.5 mM U(VI) concentration from 0 to 10 mM**

- **No interference of U(VI) on extraction and detection of Fe^{3+}**

- **However, no mass balance with U(VI)**
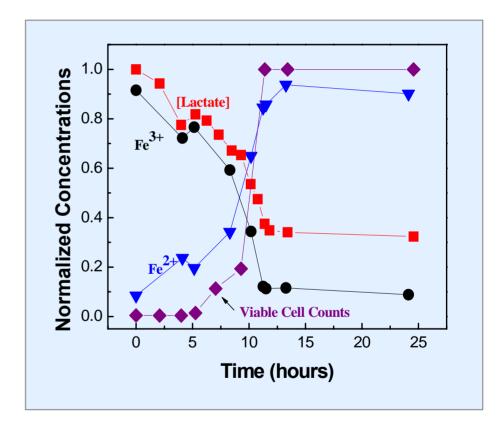 - Loss of 50% of U(VI) in stripping stage

*Mason *et al.* (1964) *Journal of Inorganic and Nuclear Chemistry,* **26,** 2271-84

Fe^{2+} and Fe^{3+} chemistry in *Shewanella alga* Biotic System

- **Anaerobic conditions**

- **Initially Fe^{3+} in presence of *S. alga***

- **Over duration of experiment, metal reducing bacteria convert insoluble Fe^{3+} to more soluble Fe^{2+}**

- **Fe^{2+} production is correlated with electron donor utilization (lactate) and cell growth**

- **Iron cycling is key to redox control of the actinides**

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Conclusions

- **Optimized conditions to successfully separate Fe^{3+} from Fe^{2+}**

- **Solvent extraction procedure works well for systems containing up to 5 mM Fe^{3+} and ~8 mM Fe^{2+}**

- **Mechanism of extraction of Fe^{3+} is by exchange of 3 protons**

- **Rate of exchange is relatively slow**
  - 1 hour for quantitative transfer of Fe^{3+}

- **Citrate and NTA cause little to no interference, whereas the strength of the EDTA complex affects Fe^{3+} extraction**

- **U(VI) does not affect extraction of Fe^{3+}**

- **Demonstrated ability to work in biotic systems**

- **On going work to correlate oxidation states of iron with oxidation states of actinides under WIPP conditions**

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