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

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

- Abiotic reduction of Np(V) to (IV) in presence of magnetite (Fe$_3$O$_4$)
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

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
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

<table>
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<tr>
<th>Complexant</th>
<th>log K</th>
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<tr>
<td>Citrate</td>
<td>11.2</td>
</tr>
<tr>
<td>NTA</td>
<td>16.00</td>
</tr>
</tbody>
</table>

Values are for I = 0.1 M at 25°C 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

![Graph showing the effect of acid concentration on Fe\(^{3+}\) and Fe\(^{2+}\) extraction.](image)

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

<table>
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<tr>
<th>Solvent</th>
<th>Relative polarity(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>0.006</td>
</tr>
<tr>
<td>heptane</td>
<td>0.012</td>
</tr>
<tr>
<td>toluene</td>
<td>0.099</td>
</tr>
<tr>
<td>water</td>
<td>1.000</td>
</tr>
</tbody>
</table>

1\(^{\text{Szymanowski et al. (1997) Hydrometallurgy, 44, 163-178}}\)

2\(^{\text{http://virtual.yosemite.cc.ca.us/smuro/orgsoltab.htm}}\)
Effect of time on HDEHP extraction

- Rate of Fe$^{3+}$ partitioning into organic phase is relatively slow
  - $\sim$ 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 \textit{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
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$^{3+}$

$$M^{3+}_{(aq)} + 3(HDEHP)_2_{(org)} \leftrightarrow M[H(\text{DEHP})_2]_3_{(org)} + 3H^+_{(aq)}$$

- Slope of graph = $\sim$-3
- Extraction by complexation with dimer form of HDEHP molecule
- Suggests exchange of 3 $H^+$ for each metal cation extracted*
  - Cation exchange

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

*Peppard et al. (1958) *Journal of Inorganic and Nuclear Chemistry* 7, 276-285
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
Effect of complexant

- Iron concentration = 0.5 mM
- Addition of Citrate, NTA or EDTA up to 10 times excess of Fe\(^{3+}\)

<table>
<thead>
<tr>
<th>Complexant</th>
<th>log K</th>
<th>Fe(^{2+})</th>
<th>Fe(^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrate</td>
<td>4.62</td>
<td>11.2</td>
<td></td>
</tr>
<tr>
<td>NTA</td>
<td>8.90</td>
<td>16.00</td>
<td></td>
</tr>
<tr>
<td>EDTA</td>
<td>14.30</td>
<td>25.1</td>
<td></td>
</tr>
</tbody>
</table>

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
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

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

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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
Conclusions

- Optimized conditions to successfully separate $\text{Fe}^{3+}$ from $\text{Fe}^{2+}$
- Solvent extraction procedure works well for systems containing up to 5 mM $\text{Fe}^{3+}$ and ~8 mM $\text{Fe}^{2+}$
- Mechanism of extraction of $\text{Fe}^{3+}$ is by exchange of 3 protons
- Rate of exchange is relatively slow
  - 1 hour for quantitative transfer of $\text{Fe}^{3+}$
- Citrate and NTA cause little to no interference, whereas the strength of the EDTA complex affects $\text{Fe}^{3+}$ extraction
- $\text{U(VI)}$ does not affect extraction of $\text{Fe}^{3+}$
- Demonstrated ability to work in biotic systems
- On going work to correlate oxidation states of iron with oxidation states of actinides under WIPP conditions
Acknowledgements

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