Why do mechanisms matter in radioactive waste management?

Or: Know your enemy

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What do we mean by mechanism?

Two examples-
Microcrystalline materials- iron oxides and sulfides
Biological transformations- bioreduction

Legacy wastes-
Pu behaviour in storage ponds
Why Do We Need to Know Mechanisms?

We often need to extrapolate, e.g. scaling up to process plant or evaluating long term wasteform performance.

Understanding physical and chemical mechanism allows realistic description and gives greater confidence in these extrapolations.

A Simple Example- Radioactivity Measurements

Count rate = 100 - 0.08 x Time
Decrease to 50% after 6.25 days

Count rate = (Count rate)\textsubscript{t=0} e^{-k \times \text{Time}}
Decrease to 50% after 8 days
But the real world is complicated

Problems- low concentrations, complex mixtures, fine particle size, heterogeneity, variability, biological activity

Concrete is heterogeneous on scales from cm to nm

SEM image of aquatic sediment
How can we study mechanism in these complex systems?

Use laboratory models to reduce variability, provide greater control, and allow the use of higher concentrations of radioelements.

This allows use of a wider range of techniques and characterisation at the molecular and near-molecular scale.

But, because we are working with simplified systems, we need to interpret the results with caution.
Microcrystalline Materials
The X-ray Absorption Spectroscopy Experiment

Use synchrotron X-ray source-monochromatic, intense (10^6 x X-ray tube)

Eject core electron from absorber atom

Outgoing photoelectron wave reflected back from neighbouring atoms

Interference pattern contains information on number, type, distance of backscatterers

Incoming X-ray photon

Double crystal monochromator

White beam

Monochromatic X-rays

Sample

I₀ → Iₜ → Iₘₐₙ

I_f
XANES (X-ray absorption near edge spectroscopy) - fingerprints oxidation state

EXAFS (extended X-ray absorption fine structure) - quantitative modelling of coordination environment (n ± 20%; r ± 0.02 Å)

Raw Spectrum

Isolated EXAFS

Fourier Transform

XANES Spectrum
Example: Uranyl Ion Reacting with Hydrous Fe Oxides

Proposed coordination environment of uranyl on the iron oxide surface

EXAFS spectroscopy gives:

<table>
<thead>
<tr>
<th>Number</th>
<th>Type</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>O</td>
<td>1.79</td>
</tr>
<tr>
<td>3</td>
<td>O</td>
<td>2.35</td>
</tr>
<tr>
<td>2</td>
<td>O</td>
<td>2.52</td>
</tr>
<tr>
<td>1</td>
<td>Fe</td>
<td>3.42</td>
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</tbody>
</table>

From: Waite et al., Geochimica et Cosmochimica Acta 58, 5465-5478 (1994)
Why Iron Sulfides?

Important and widespread mineral phases in anaerobic conditions such as aquatic sediments

Microcrystalline with high surface area and redox active surface

Originates from use of alternative electron acceptors in bacterial metabolism

\[
\begin{align*}
\text{Fe(III)} & \rightarrow \text{Fe(II)} \\
\text{SO}_4^{2-} & \rightarrow \text{S}^{2-} \\
\text{Fe}^{2+} + \text{S}^{2-} & \rightarrow \text{FeS}
\end{align*}
\]

Microbiology and Radioactivity (eds M J Keith-Roach and F R Livens), Elsevier Dec 2001
Removal of $UO_2^{2+}$ and $NpO_2^+$ from Solution by FeS

Uranium uptake is almost quantitative and is independent of solution concentration.

Neptunium uptake is relatively low but independent of solution concentration.
Reactions with mineral surfaces studied with XANES spectroscopy

Uranyl reacted with Fe phases

Neptunyl reacted with FeS
Surface reactions with FeS studied by EXAFS

Uranium

Aqueous

Increasing [U]

Neptunium

Increasing [Np]
# EXAFS Fitting Parameters

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Number, Type</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4500 ppm</td>
<td>2 O</td>
<td>1.81</td>
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<tr>
<td></td>
<td>4 O</td>
<td>2.40</td>
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<tr>
<td>24000 ppm</td>
<td>2 O</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td>2 O</td>
<td>2.14</td>
</tr>
<tr>
<td></td>
<td>4 O</td>
<td>2.36</td>
</tr>
<tr>
<td>113000 ppm</td>
<td>2 O</td>
<td>1.83</td>
</tr>
<tr>
<td>Uranium</td>
<td>1 O</td>
<td>2.07</td>
</tr>
<tr>
<td></td>
<td>5 O</td>
<td>2.31</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Number, Type</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>650 ppm</td>
<td>4 O</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>3 S</td>
<td>2.63</td>
</tr>
<tr>
<td>1625 ppm</td>
<td>4 O</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>3 S</td>
<td>2.61</td>
</tr>
<tr>
<td>6500 ppm</td>
<td>4 O</td>
<td>2.26</td>
</tr>
<tr>
<td>Neptunium</td>
<td>3 S</td>
<td>2.64</td>
</tr>
</tbody>
</table>

Proposed coordination environment of Np on FeS surface

Microbiological Transformations
Bacterial Redox Processes - Geobacter sulfurreducens

Known transformations:
- $\text{TcO}_4^- \text{ (soluble)} \rightarrow \text{TcO}_2.2\text{H}_2\text{O} \text{ (insoluble)}$
- $\text{UO}_2^{2+} \text{ (soluble)} \rightarrow \text{UO}_2.2\text{H}_2\text{O} \text{ (insoluble)}$

So how does Np ($\text{NpO}_2^+$ is potentially mobile) behave?
Effect of G. sulfurreducens on NpO₂⁺
• Assumed mechanism: $2e^- \text{ reduction } U(\text{VI}) \rightarrow U(\text{IV})$

• Alternative mechanism: $1e^- \text{ reduction } U(\text{VI}) \rightarrow U(\text{V})$
  - $U$ disproportionates $\rightarrow U(\text{VI}) + U(\text{IV})$
  - Cycle of $U(\text{VI})$ reduction until nearly all $U(\text{IV})$

\[ \text{UO}_2^{2+} \rightarrow \text{UO}_2^{2+} + \text{U}^{4+} \]
Identification of U(V) by EXAFS Spectroscopy

Abundance of Different U Species
Plutonium in Ponds
Observations-

Discharges of Pu from ponds may be difficult to predict
These effluents need to be carefully managed
What is in the ponds?
- Corroded Magnox sludge (CMS)
- Water
- NaOH to bring pH to 11

\[
\begin{align*}
\text{Mg} + 2 \text{NaOH} & \rightarrow \text{Mg(OH)}_2 + 2 \text{Na}^+ \\
\text{NaOH} + \text{CO}_2 & \rightarrow \text{NaHCO}_3 \\
\text{Mg(OH)}_2 + \text{CO}_3^{2-} & \rightarrow \text{MgCO}_3 + 2 \text{OH}^- 
\end{align*}
\]

Key Questions-
- Is Pu in solution or particle associated?
- What is the nature of the particles?
- What is the nature of Pu solution species?
- What are the effects of effluent treatments?

Also-
- How do we immobilise the Magnox sludges?

What happens to the effluents?
- Effluent pH 11
- Sand bed filter
- Adjust to pH 7 with CO₂ gas
- Zeolite ion exchange
- Discharge to sea
ESEM Imaging of CMS Simulant

Two morphologies
Wide distribution of particle sizes
XRD- brucite and arctinite (MgCO₃·Mg(OH)₂·3H₂O)
Solubility, filterability, interconversion?
What influences Pu solubility?

Use filtration (0.22 µm) to define “solubility”

Factorial experiment allows quantitative assessment of different controls on Pu

Analysis of variance

% of Pu(IV) retained on a 0.22 µm filter

<table>
<thead>
<tr>
<th>Condition</th>
<th>pH 11</th>
<th>pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ CMS</td>
<td>100</td>
<td>75</td>
</tr>
<tr>
<td>- CMS</td>
<td>75</td>
<td>50</td>
</tr>
<tr>
<td>+ Si</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>+ CMS + Si</td>
<td>75</td>
<td>50</td>
</tr>
<tr>
<td>pH 7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
We need to understand the mechanisms underlying waste behaviour.

There are complexities in defining the behaviour of the actinides, arising both from the chemical complexity of the actinides and from the complexity of heterogeneous waste systems.

Using modern spectroscopic and analytical techniques it is possible to make progress.

We have a good deal of work still to do, especially for the transuranic elements.

It would be very helpful to have robust, fundamental models (e.g. quantum) of these difficult systems.