Why do mechanisms matter in radioactive waste management?

Or: Know your enemy

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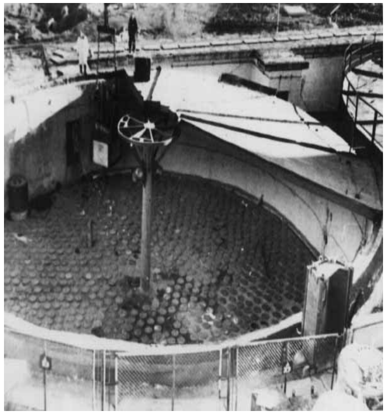
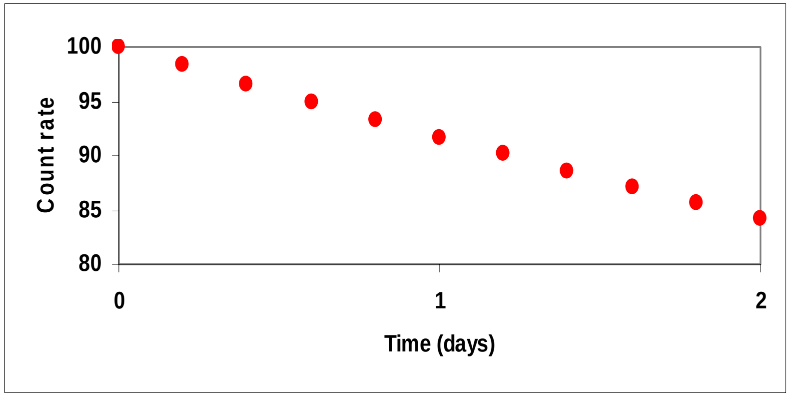


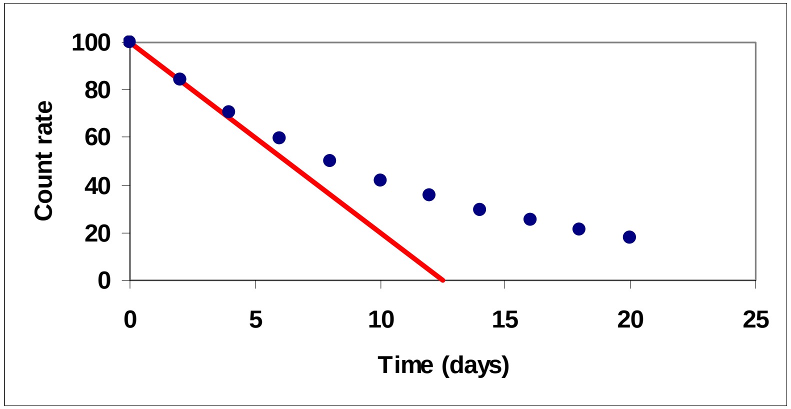
Why Do We Need to Know Mechanisms?

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

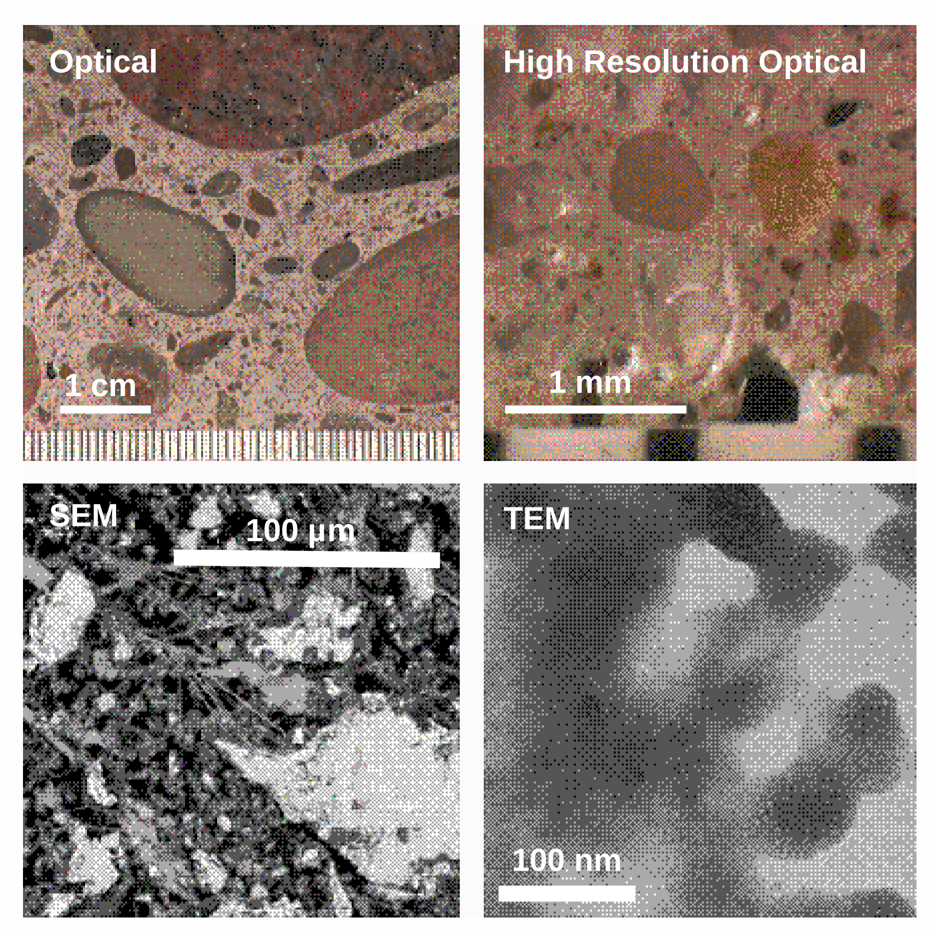
Decrease to 50% after 6.25 days

Count rate = (Count rate)$_{t=0}$ e $^{-k \times Time}$

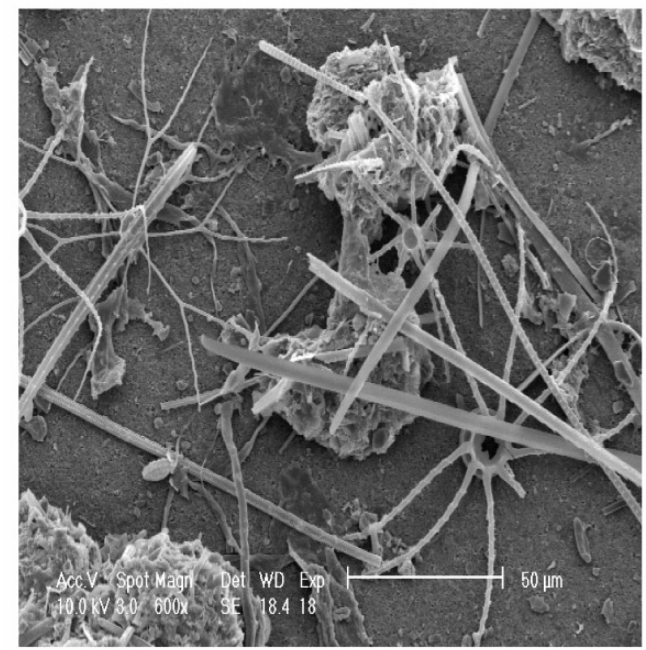
Decrease to 50% after 8 days

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

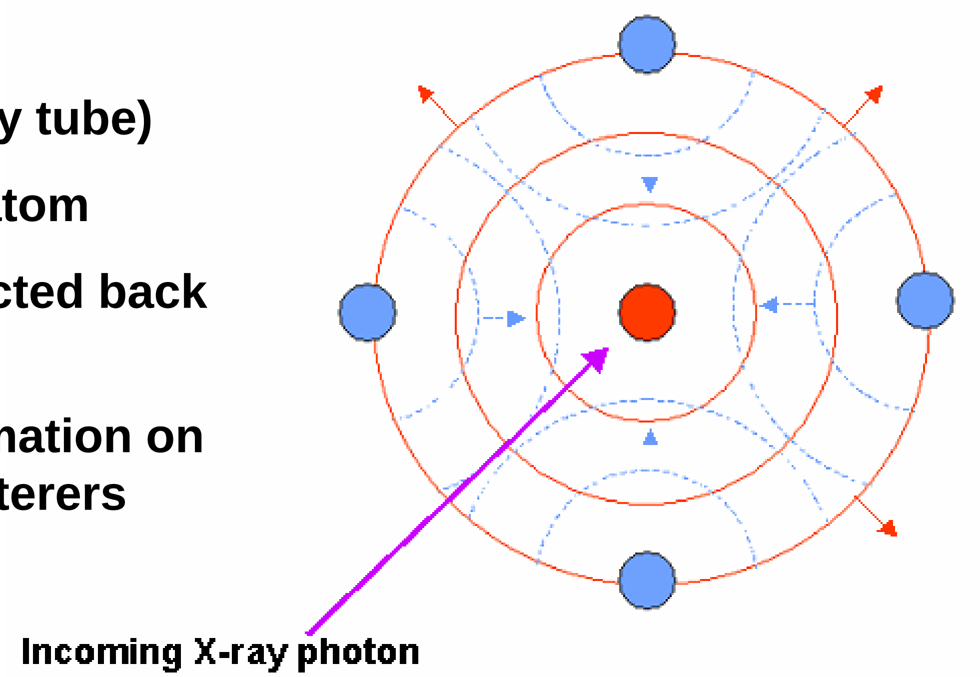
NpO_2^+

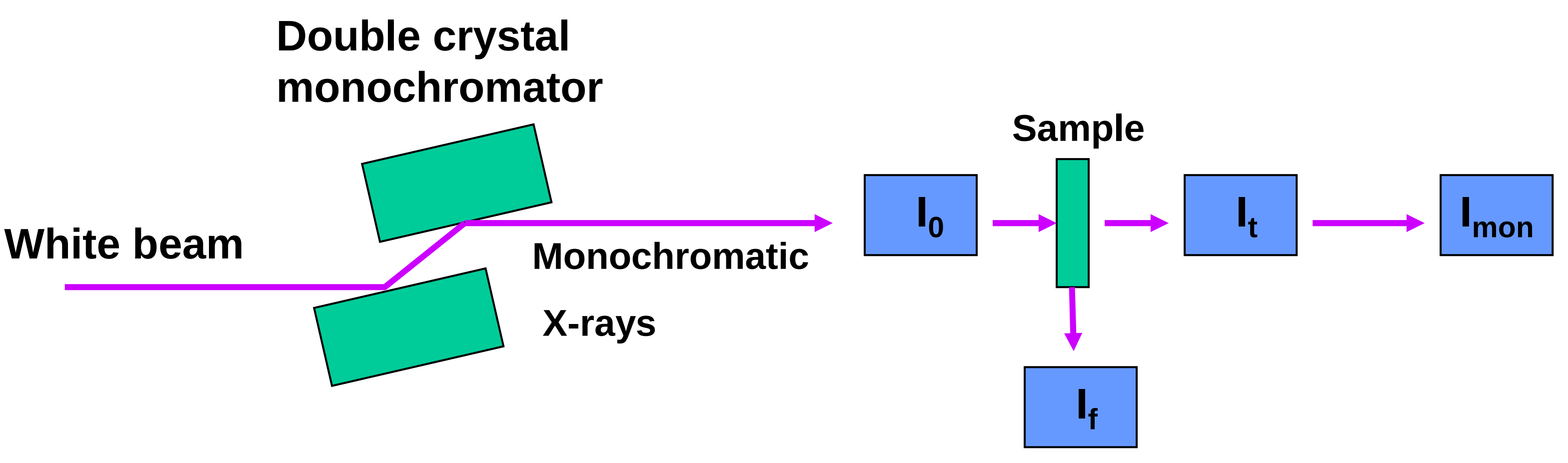
NpO_2^{2+}

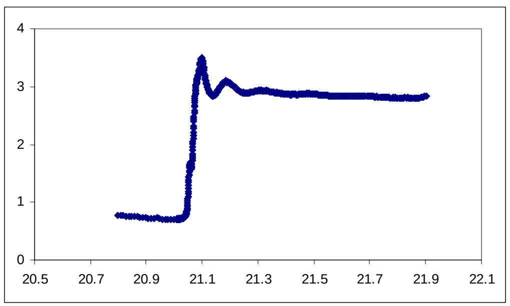
Microcrystalline Materials

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**

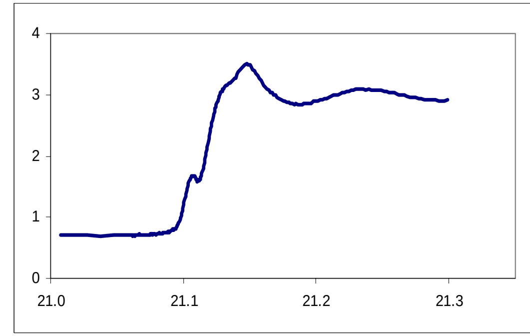




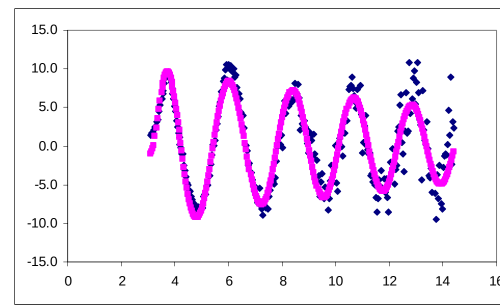


Raw Spectrum

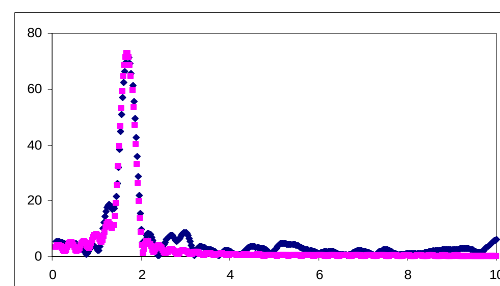
XANES (X-ray absorption near edge spectroscopy)- fingerprints oxidation state



XANES Spectrum



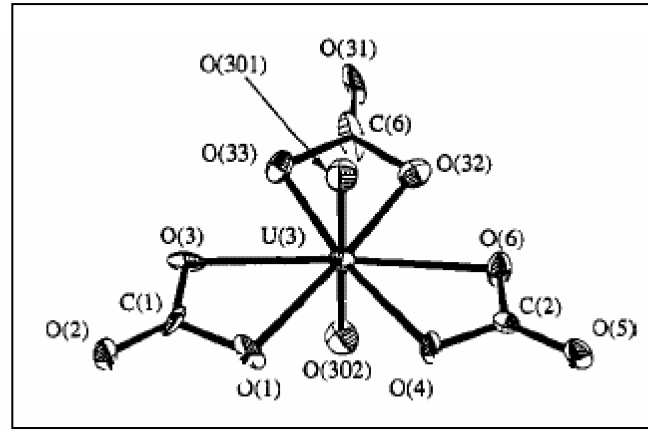
Isolated EXAFS



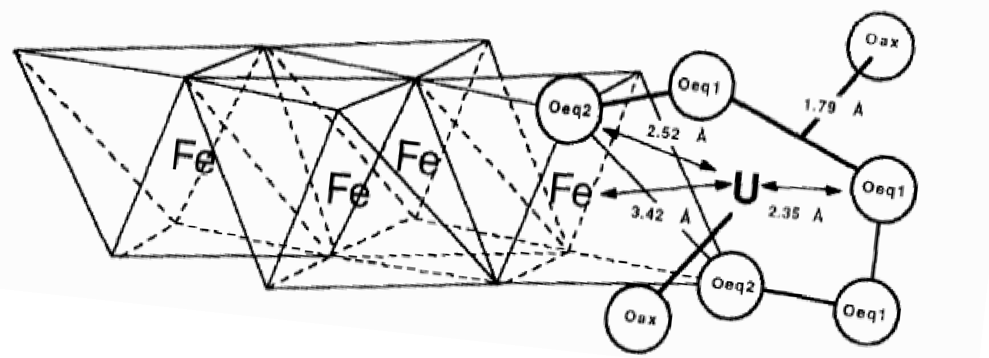
Fourier Transform

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

Example- Uranyl Ion Reacting with Hydrous Fe Oxides



Proposed coordination environment of uranyl on the iron oxide surface



EXAFS spectroscopy gives:

Number	Type	Distance (Å)
2	O	1.79
3	O	2.35
2	O	2.52
1	Fe	3.42

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

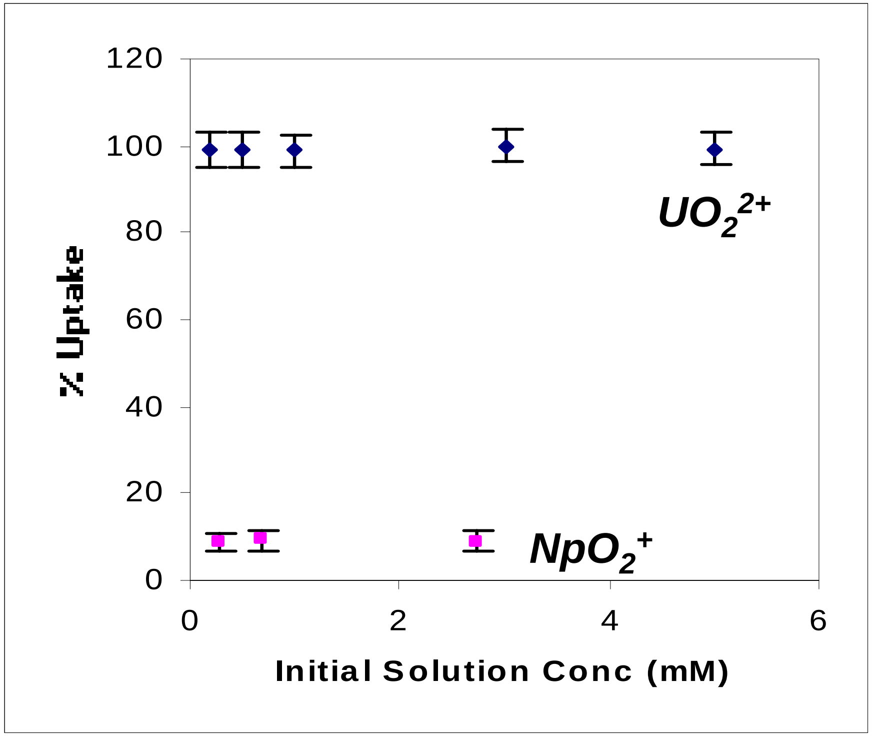
Fe(III)$\rightarrow$ Fe(II)

$SO_4^{2-} \rightarrow S^{2-}$

$Fe^{2+} + S^{2-} \rightarrow FeS$

Microbiology and Radioactivity (eds M J Keith-Roach and F R Livens), Elsevier Dec 2001

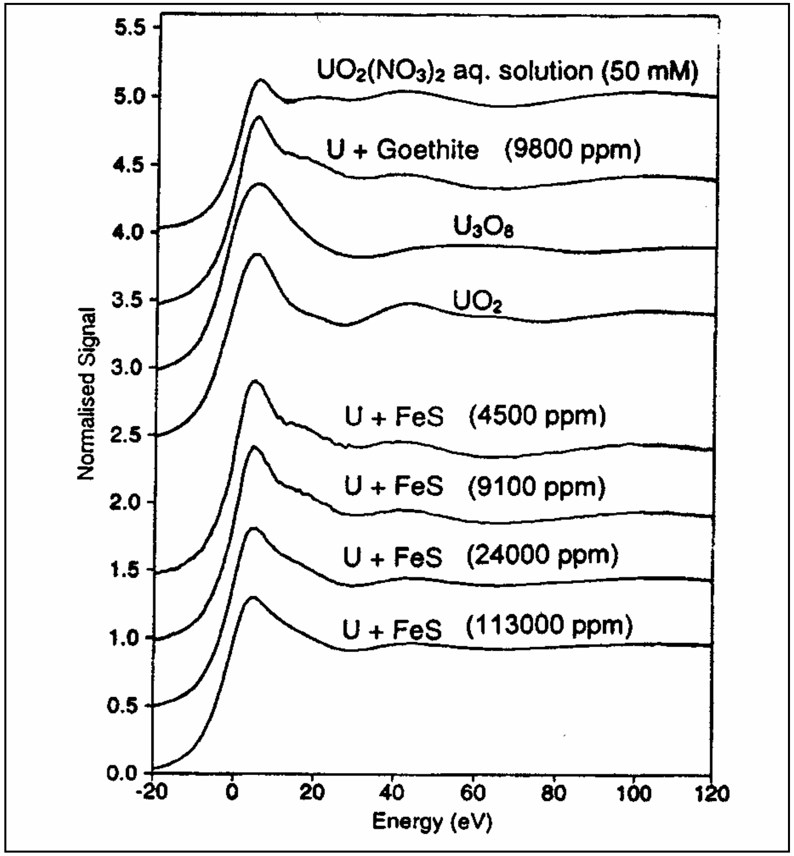
Removal of UO_2^{2+} and NpO_2^{+} from Solution by FeS



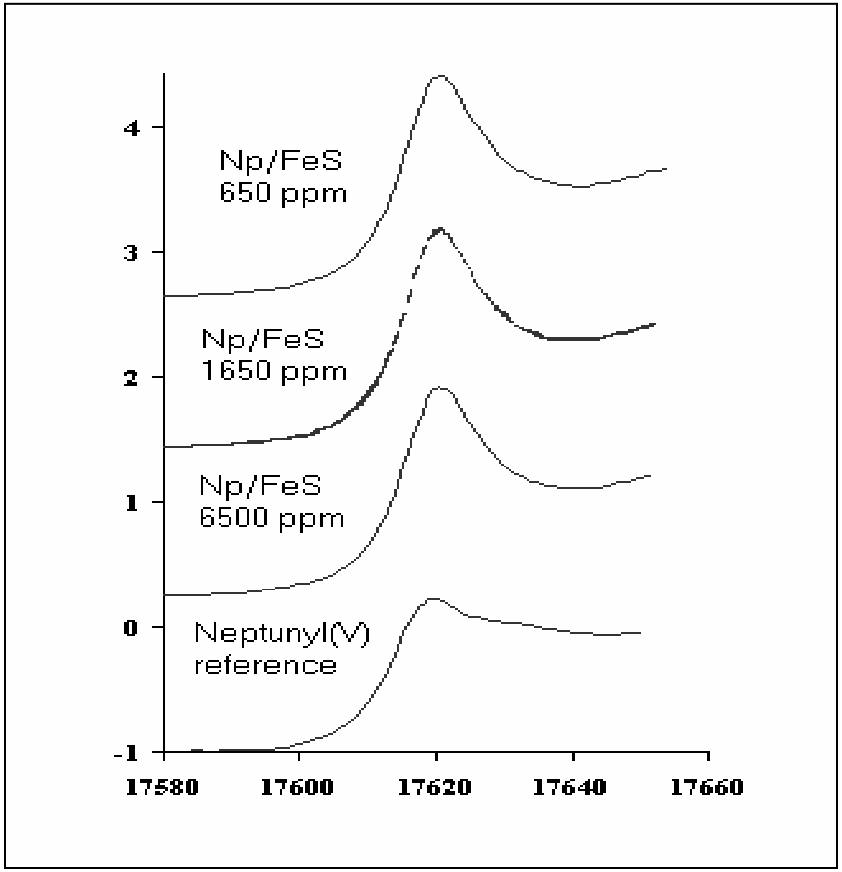
Uranium uptake is almost quantitative and is independent of solution concentration

Neptunium uptake is relatively low but independent of solution concentration

Reactions with mineral surfaces studied with XANES spectroscopy



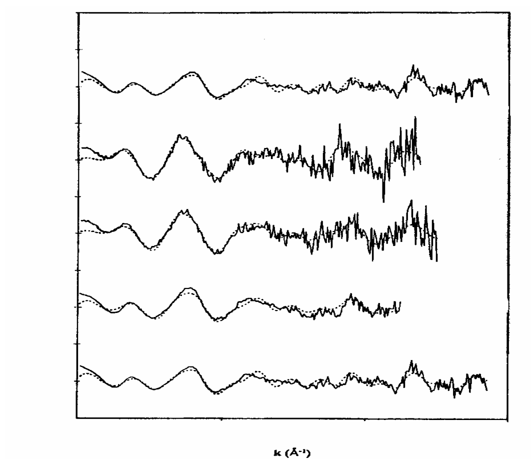
Uranyl reacted with Fe phases

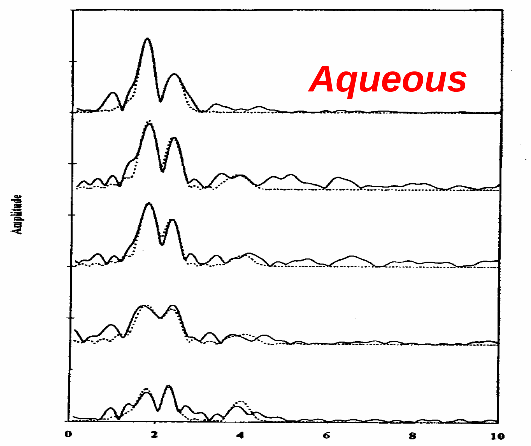


Neptunyl reacted with FeS

Surface reactions with FeS studied by EXAFS

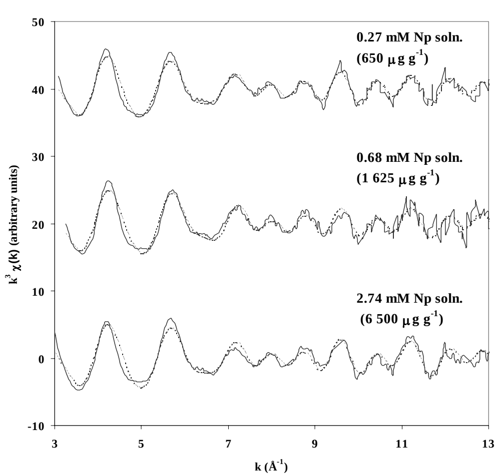
Uranium

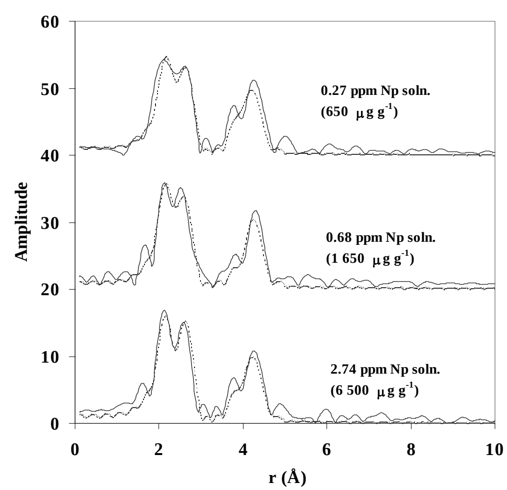




Increasing [U]

Neptunium



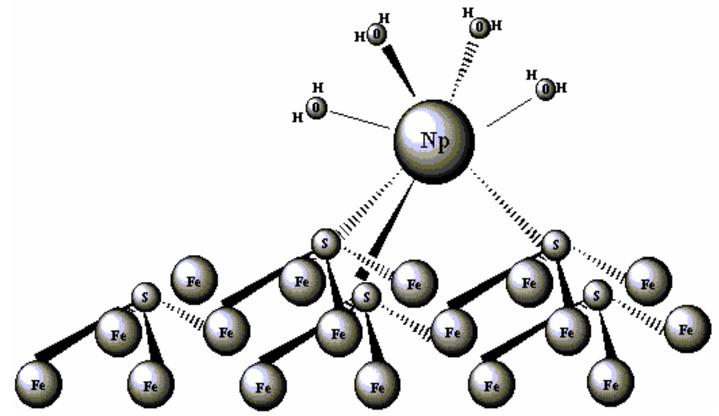


Increasing [Np]

EXAFS Fitting Parameters

Concentration	*Number,Type*	*Distance (Å)*
4500 ppm	2 O	1.81
	4 O	2.40
24000 ppm	2 O	1.81
	2 O	2.14
	4 O	2.36
113000 ppm	2 O	1.83
Uranium	1 O	2.07
	5 O	2.31

Concentration	*Number,Type*	*Distance (Å)*
650 ppm	4 O	2.25
	3 S	2.63
1625 ppm	4 O	2.25
	3 S	2.61
6500 ppm	4 O	2.26
Neptunium	3 S	2.64



Proposed coordination environment of Np on FeS surface

L N Moyes *et al*., Environmental Science and Technology, 34, 1062-1068 (2000); Environmental Science and Technology, 36, 179-183 (2002)

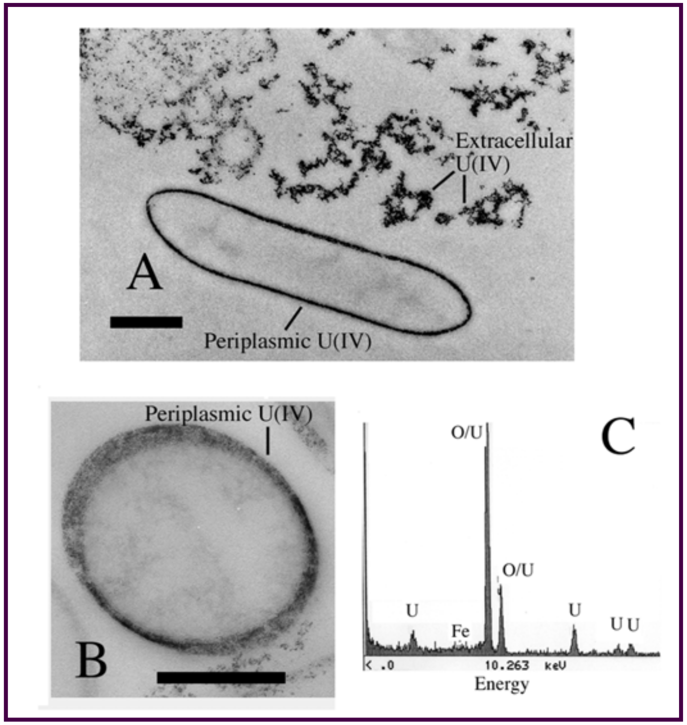
Microbiological Transformations

Bacterial Redox Processes- Geobacter sulfurreducens

Known transformations-

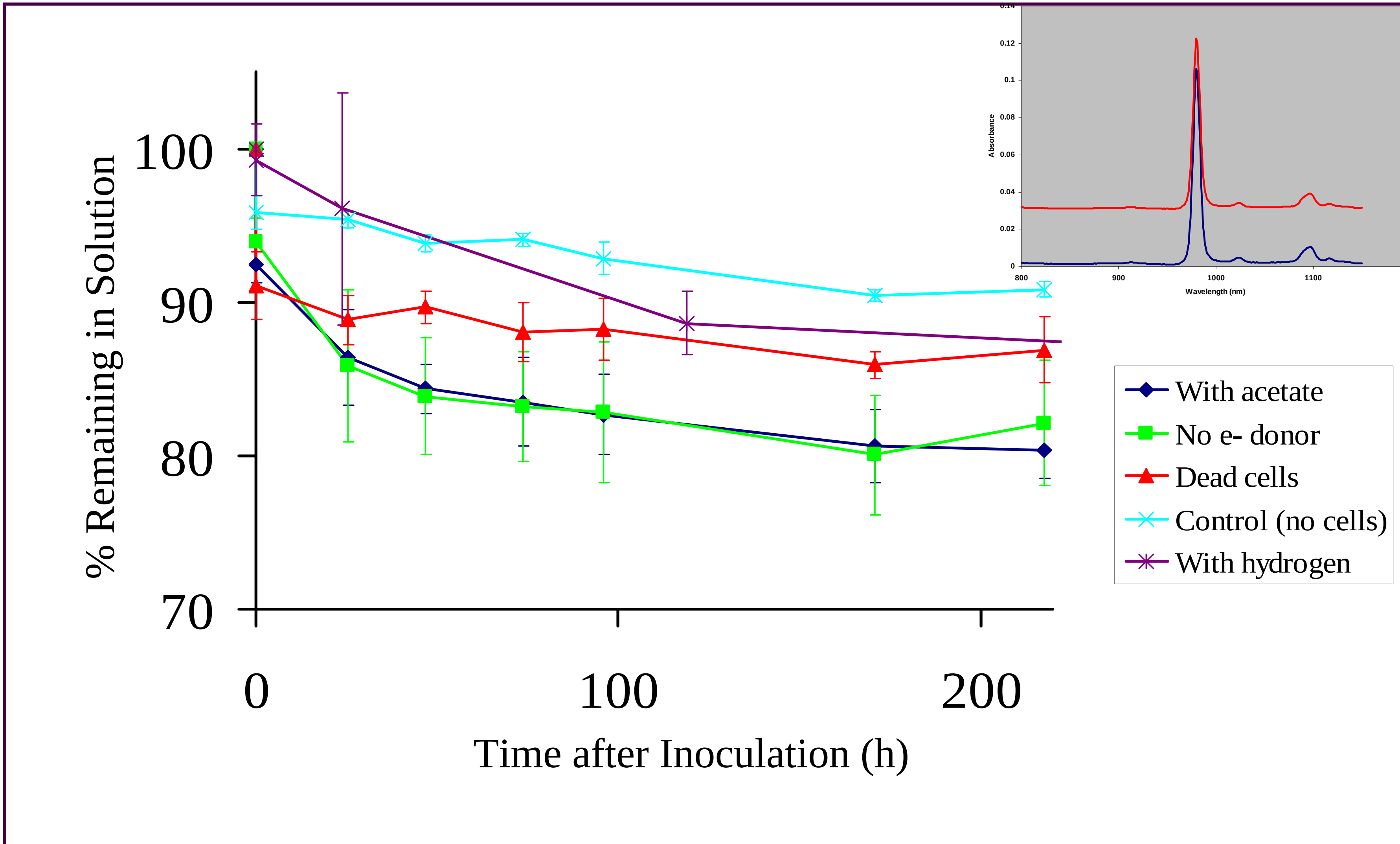
TcO_4^- (soluble) ⟶ $TcO_2.2H_2O$ (insoluble)

UO_2^{2+} (soluble) ⟶ $UO_2.2H_2O$ (insoluble)



So how does Np (NpO_2^+ is potentially mobile) behave?

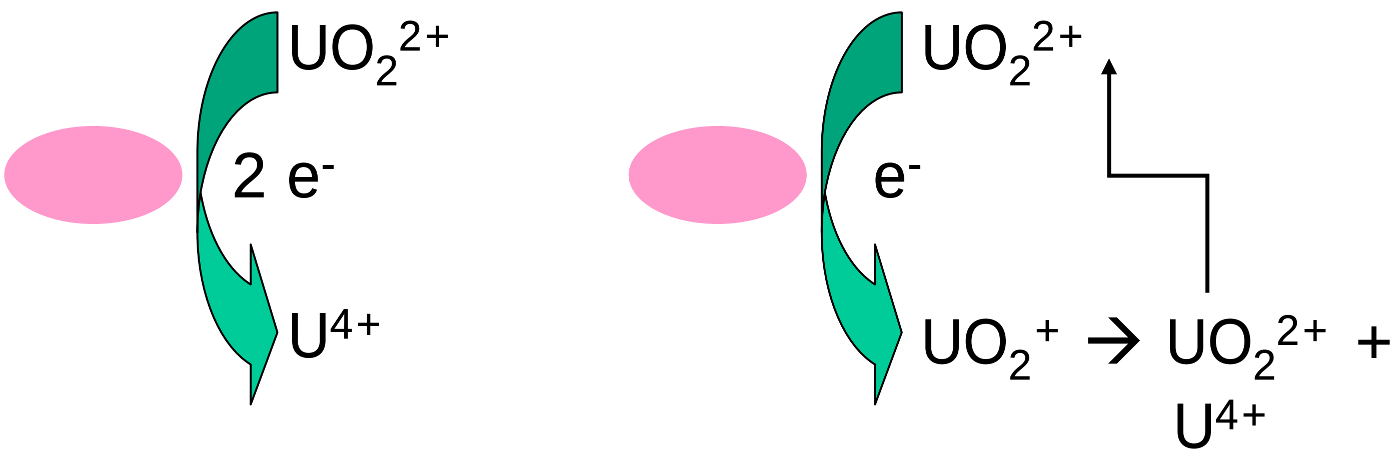
Effect of G. sulfurreducens *on* NpO_2^+



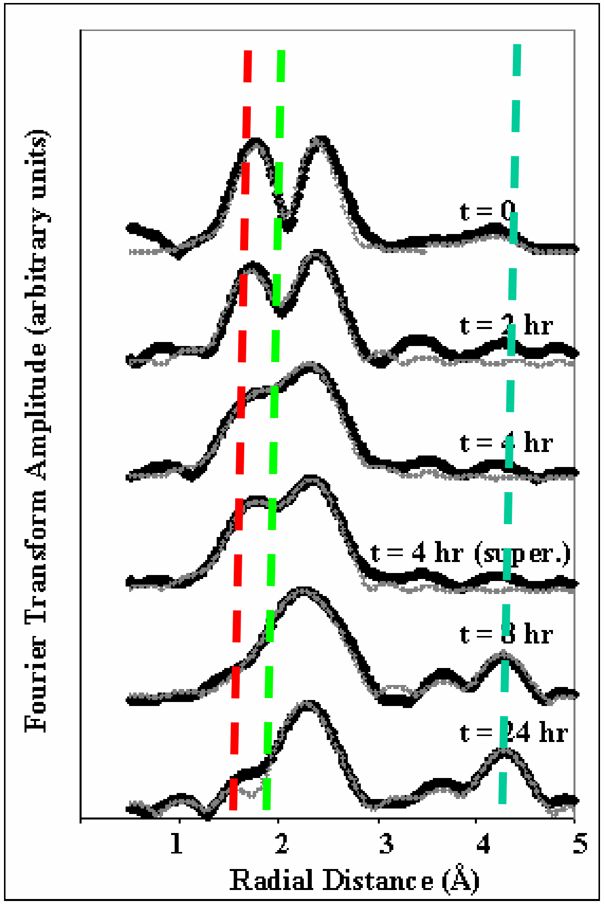
Chemical Transformations

- **Assumed mechanism: 2e⁻ reduction U(VI) → U(IV)**

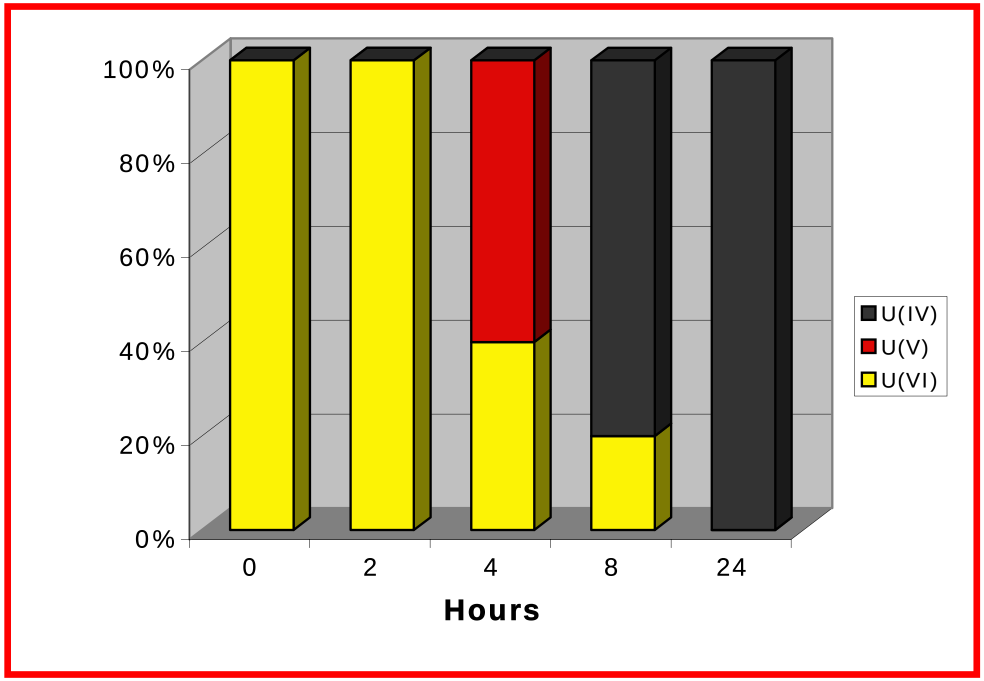
- **Alternative mechanism: 1 e⁻ reduction U(VI) → U(V)**
  - **U disproportionates → U(VI) + U(IV)**
  - **Cycle of U(VI) reduction until nearly all U(IV)**



Identification of U(V) by EXAFS Spectroscopy



U(VI)
U(V)
U(IV)



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

Useful Stuff and Important Questions

What is in the ponds?

Corroded Magnox sludge (CMS)

Water

NaOH to bring pH to 11

$$Mg + 2\,NaOH \longrightarrow Mg(OH)_2 + 2\,Na^+$$

$$NaOH + CO_2 \longrightarrow NaHCO_3$$

$$Mg(OH)_2 + CO_3^{2-} \longrightarrow MgCO_3 + 2\,OH^-$$

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 CO_2 gas

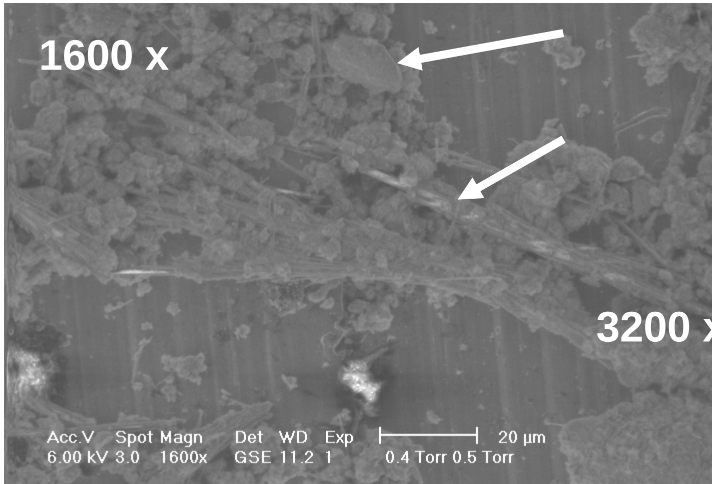
↓

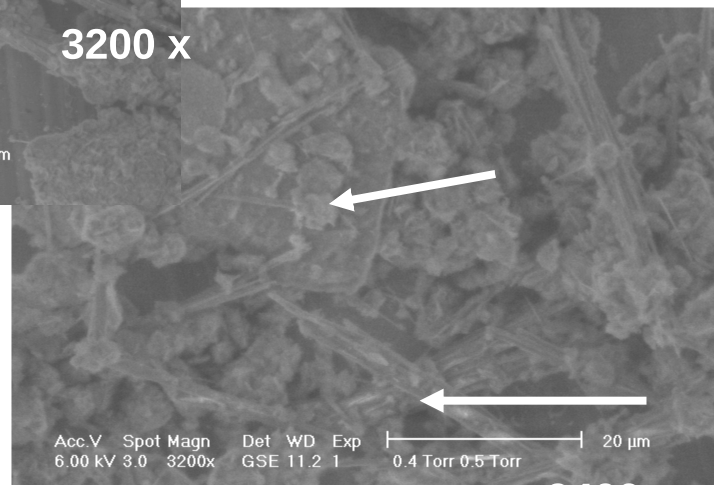
Zeolite ion exchange

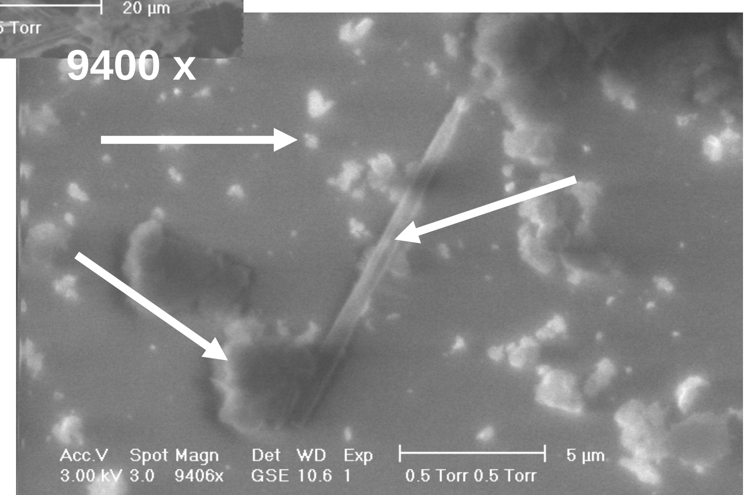
↓

Discharge to sea

ESEM Imaging of CMS Simulant







Two morphologies

Wide distribution of particle sizes

XRD- brucite and artinite ($MgCO_3.Mg(OH)_2.3H_2O$)

Solubility, filterability, interconversion?

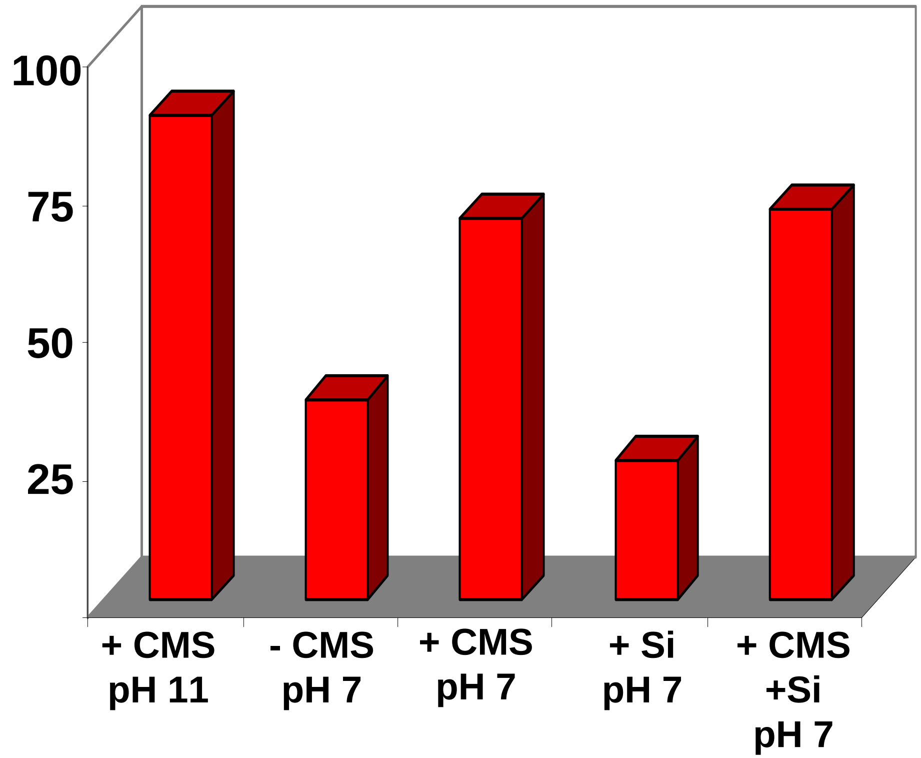
What influences Pu solubility?

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



Conclusions

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