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Characterization and Assessment of Arsenic Mineralogy using Synchrotron Radiation

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John Rowson, Areva Resources Canada Inc.

Acknowledgements

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Canadian Light Source Inc.

Mission Statement: *To advance scientific and industrial capabilities ….*

Techniques Available

- X-ray diffraction and scattering
- X-ray fluorescence imaging and microscopy at various spatial scales
- X-ray Absorption Spectroscopy (XAS) at many energies

What questions can we answer

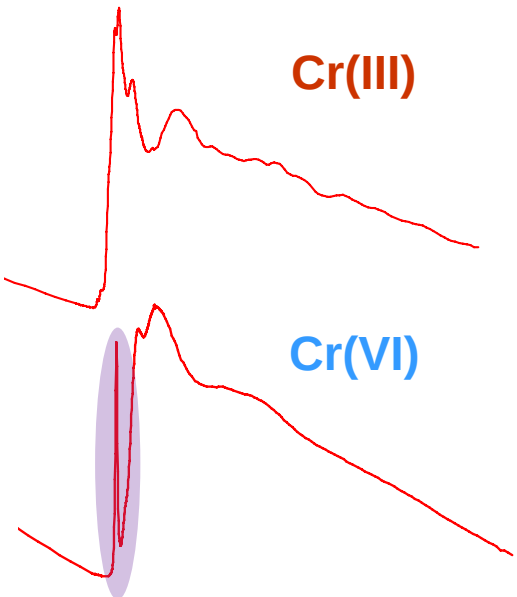
- Will the contaminant bind with soil constituents or is it mobile
- Is the species stable or labile
- What is the compounds bioavailability or toxicity

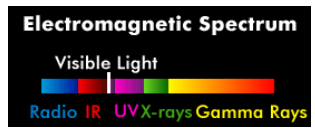
main experimental hall

Speciation Using X-ray Absorption Spectroscopy (XAS)

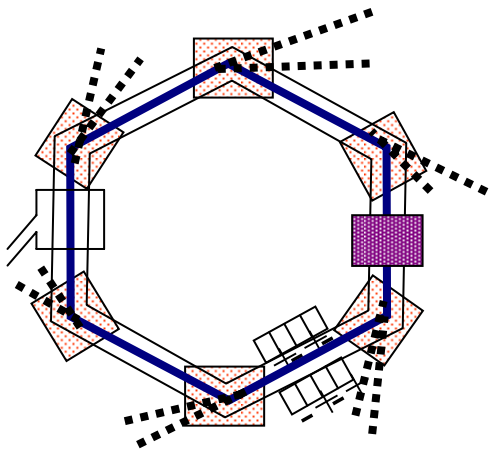
X-ray Absorption Spectroscopy is a valuable tool in environmental chemistry because of these characteristics,

- can analyze any state of matter, almost any sample - wet, dry, amorphous, etc.;
- minimal sample preparation
  - *in-situ* studies (no extraction artifacts);
- element selective detection and oxidation states;
- low concentrations (~ppm and up)
- X-ray Fluorescence can provide spatial mapping (micron scale) of samples





Properties of Synchrotron Radiation



- high photon flux
- broad spectral range
- high polarization
- natural collimation
- small spot size
- stability
- ring structure allows multiple users

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Metal Contamination

Rules of Engagement for Remediation:

- Do not make it worse
  - Do not make a large volume of waste from a small volume
  - Do not mobilize the contaminant
  - THINK before you kill (any micro-organisms)
- Do not go against geochemical gradients
- Pay attention to acid/base and oxidation/reduction chemistry
- Identify buffers (and their extent)
- Manage co-precipitation reactions
- Are there natural analogues that support the argument that the system will be stable in the long term ?
- Establish a site conceptual model that addresses: ❶ solid phase speciation
  ❷ scaling issues

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Site Characterization is Important

- Toxicological concerns depend on bioavailability
- Bioavailability is dependant, not on total elemental concentrations, but molecules
- Thorough site characterization identifies the concentration of metals present as well as their oxidation states and, if possible, their chemical speciation

toxic red mud

- Is any action required ?
- How much unnecessary remediation is done because of incomplete information ?

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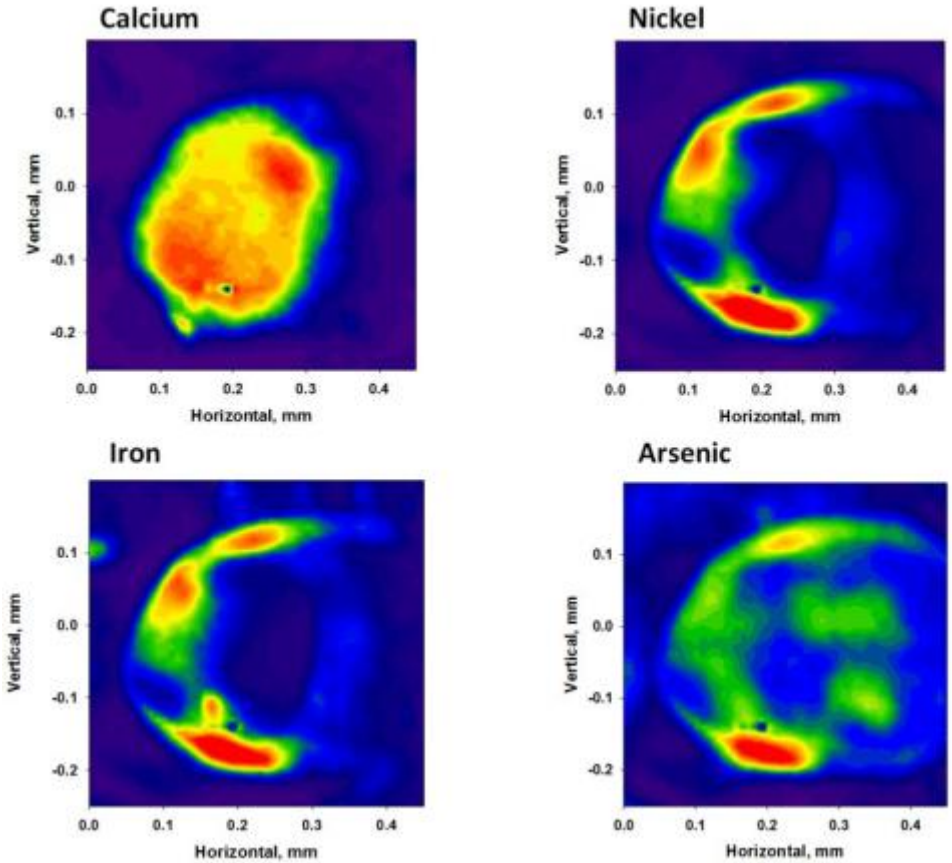
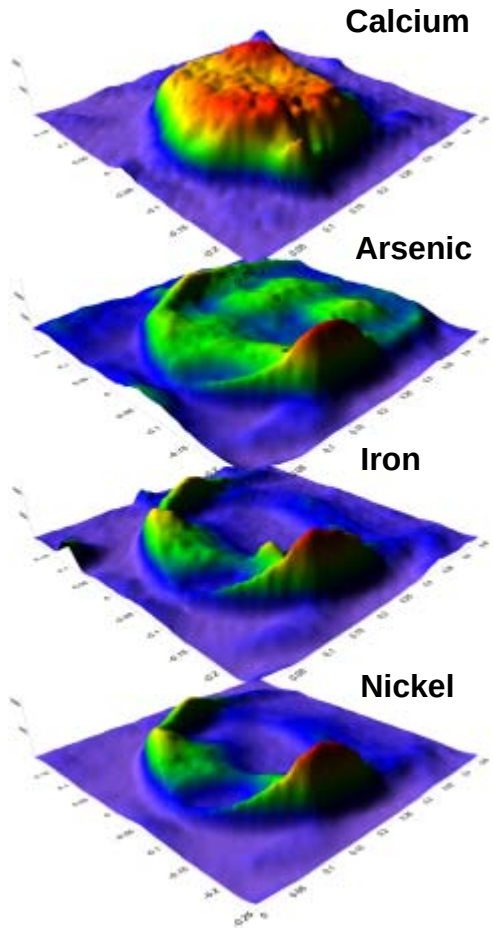
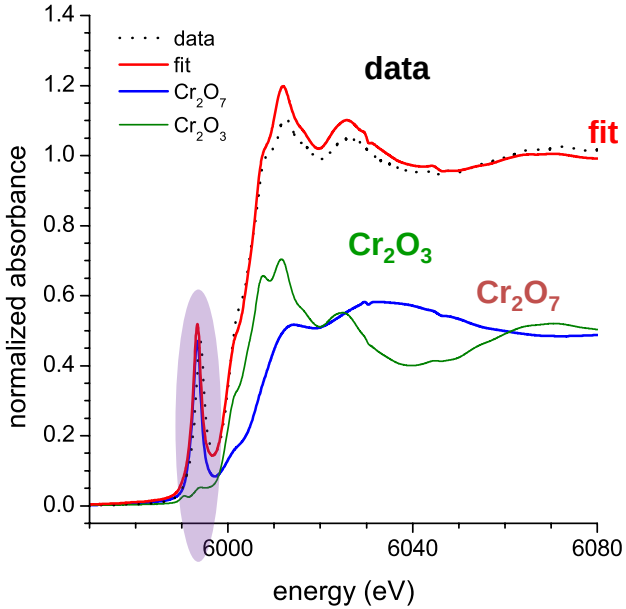
Samples from a Uranium Mine Tailings Management Facility

XRF maps of a gypsum nodule



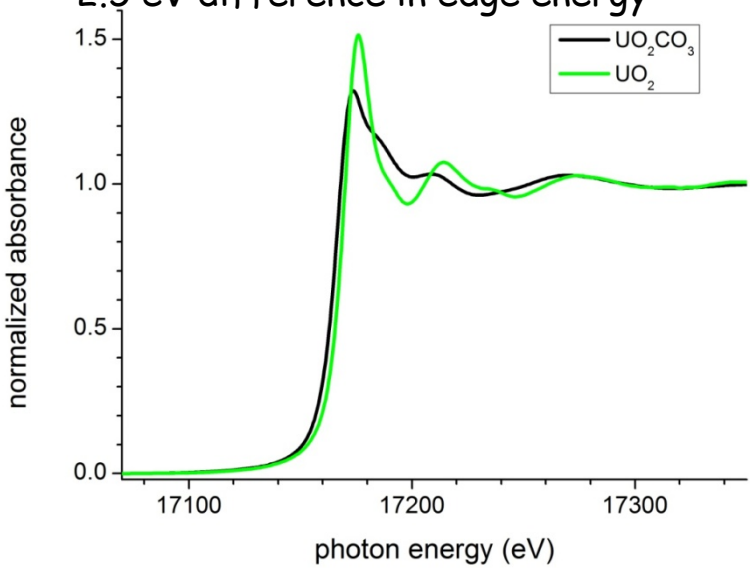


X-ray Absorption Near Edge Structure (XANES) Spectroscopy

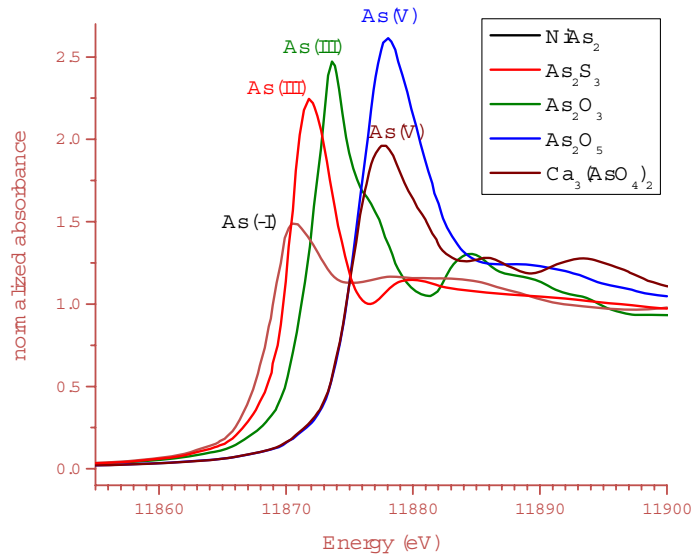


XANES Spectra of Cr(III) and Cr(VI). The large pre-edge peak is indicative of Cr(VI).

XANES Spectra of $U(VI)O_2CO_3$ and $U(IV)O_2$
~ 2.5 eV difference in edge energy



Arsenic has large differences in edge position



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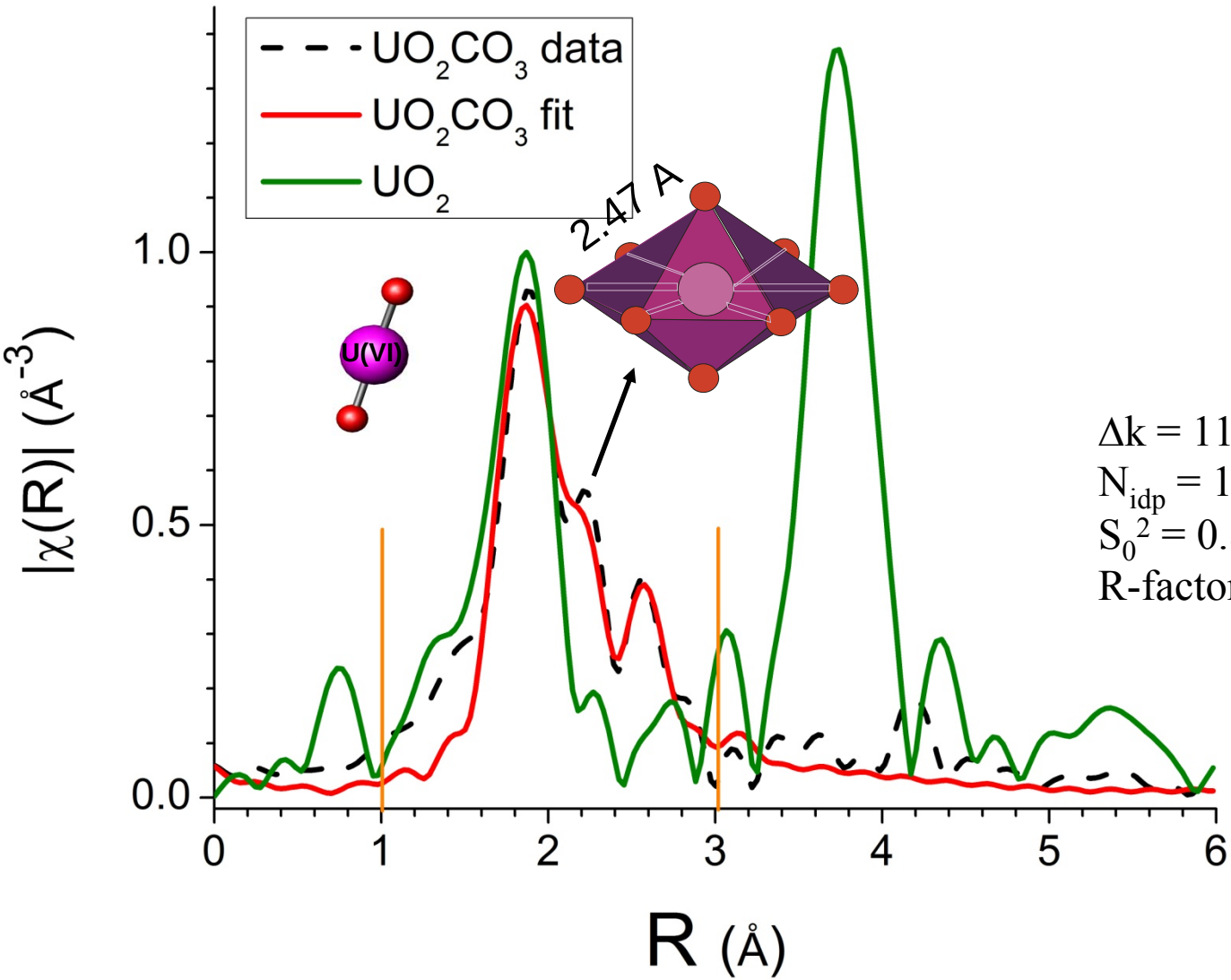
EXAFS Spectroscopy is a Powerful Tool for Determining Contaminant Bonding

EXAFS – Extended X-ray Absorption Fine Structure



$\Delta k = 11.8$ Å^{-1}; $\Delta R = 2.0$ Å

$N_{idp} = 14$, varied = 8

$S_0^2 = 0.88$, $\Delta E_0 = 6.1 \pm 0.2$ eV

R-factor = 6.5%

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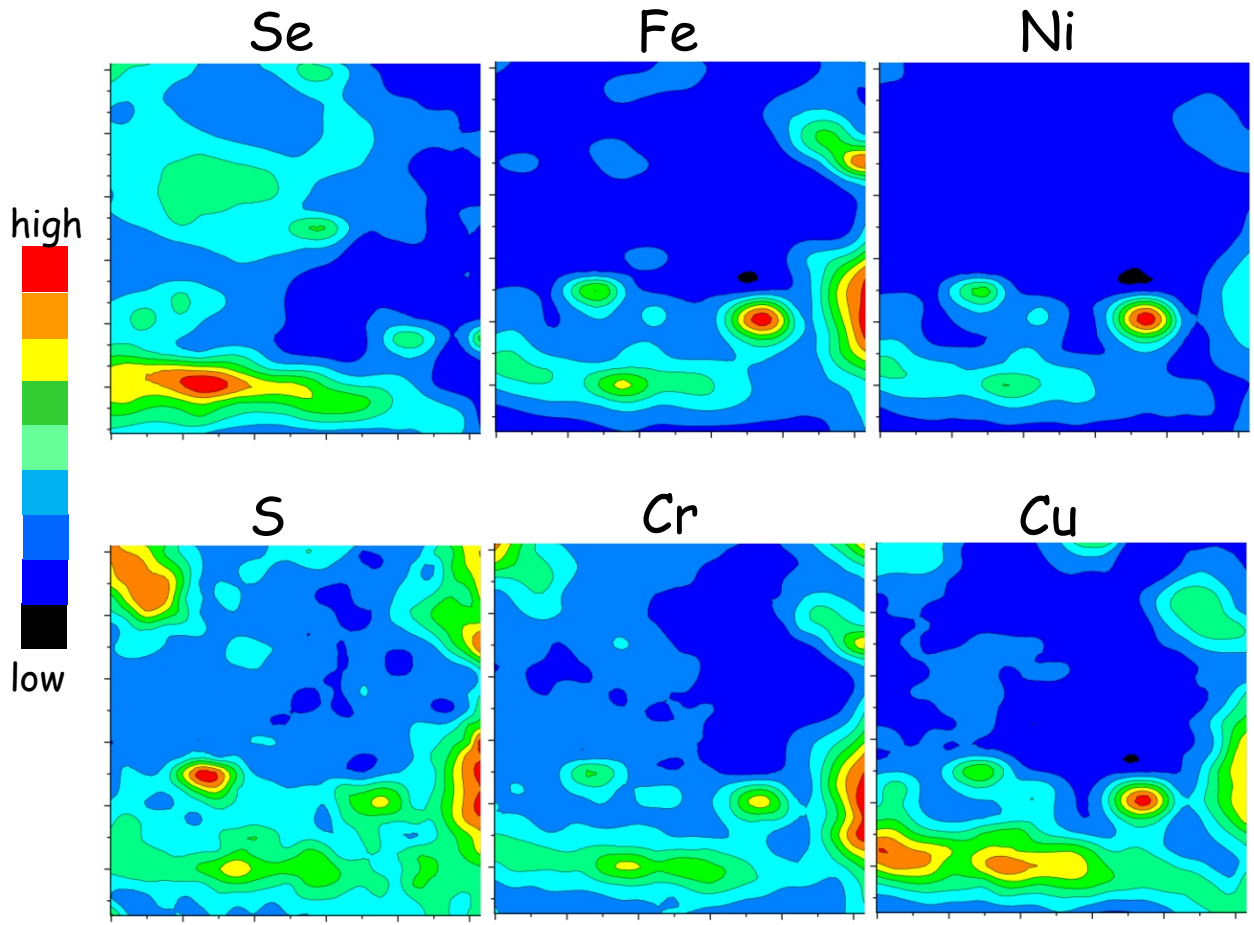
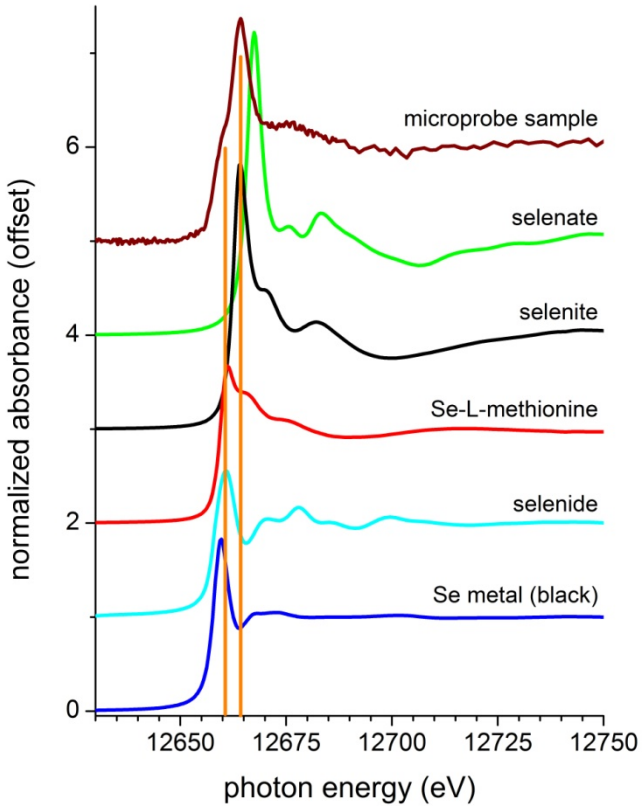
XRF Microprobe Measurements of Selenium in Coal





Selenium is associated with elevated concentrations of other metals and sulfur. Bulk spectroscopy indicates the presence of selenite and other reduced forms of selenium

Arsenic at McClean Lake

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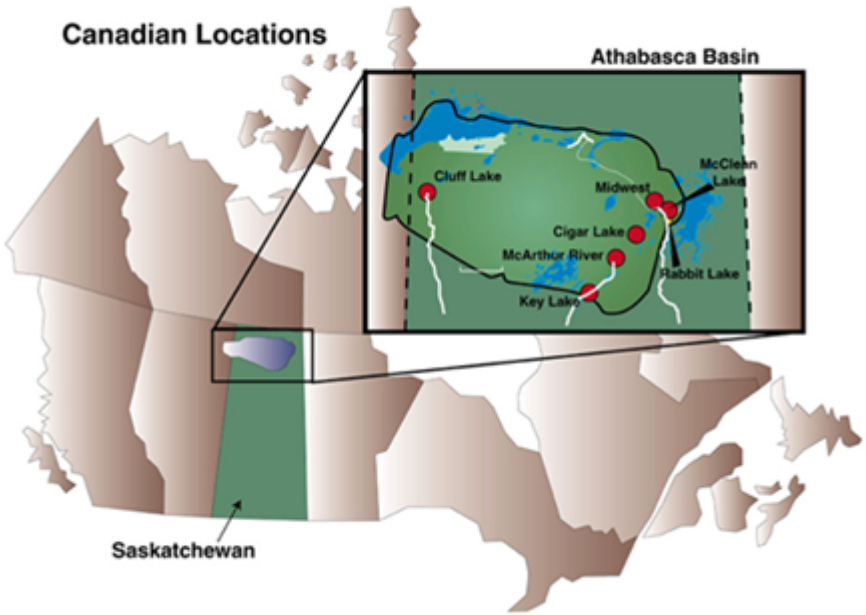
33% of the world production of U is mined in the Athabasca basin of northern Saskatchewan

Uranium ore containing elevated concentrations of arsenic (up to 2 wt %) are processed at the McClean Lake operation



Areva operates the JEB Tailings Management Facility (TMF) as an integral component of its uranium mining operations.

The Challenge:

Ensure long term storage stability of deposited tailings in the JEB TMF.

The Tailings Management Facility

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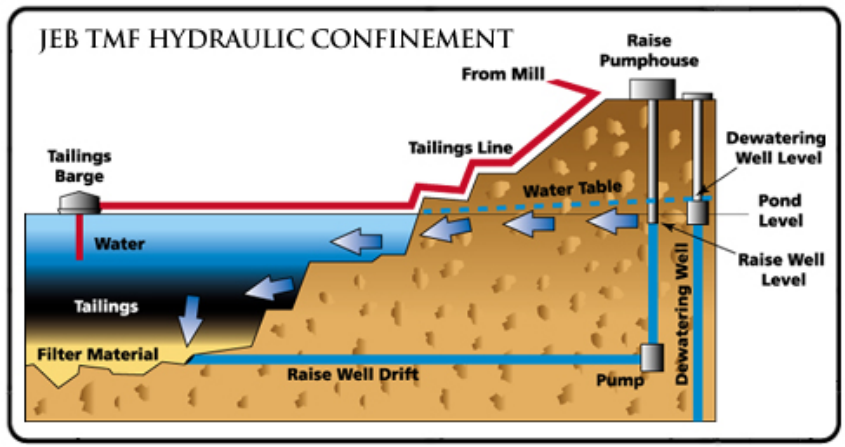
The tailings are disposed of below the water table in a redesigned and engineered mined out pit

The JEB TMF has been designed to minimize the migration of soluble constituents from the facility using 2 key strategies:

- physical containment
  - maintained through hydraulic isolation
- geochemical controls
  - in order to predict the long term release of potential contaminants

Areva Resources strategy focused on understanding Arsenic Speciation in the tailings



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Laboratory Investigations

Laboratory and Theoretical Test Work
was performed on the,

- chemistry of neutralized raffinate solutions
- mineralogy of precipitated solids
- geochemical modeling of the raffinate neutralization process from pH 2 to 8

- the stability of scorodite [$FeAsO_4.2H_2O$] in water is highly dependant on the stability of the co-existing iron (hydr)oxide phase
- arsenate appears to stabilize ferrihydrite
- modeling indicates that arsenic concentrations are controlled by saturation with a poorly crystalline scorodite

Geochemical Controls

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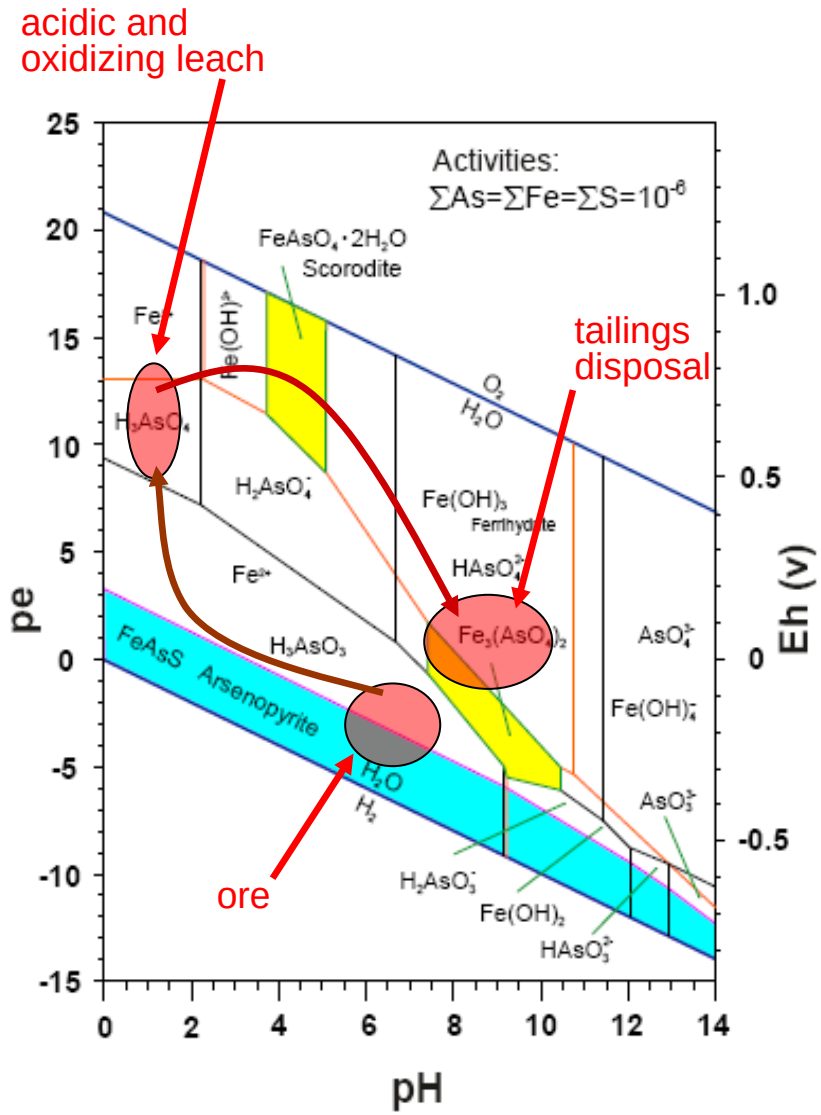
The use of coprecipitation with Fe(III) has been used to remove arsenic in hydrometallurgical solutions

There are many uncertainties associated with the technology

- $[As]_{initial}$
- presence of other oxidants or reductants

- the stability of secondary phases

  - a related concern is that current arsenic pore water levels are achieved due to the slow kinetics of arsenic transformation and release over time



Eh-pH diagram for As-Fe-S-H_2O.

Monitoring and Validation

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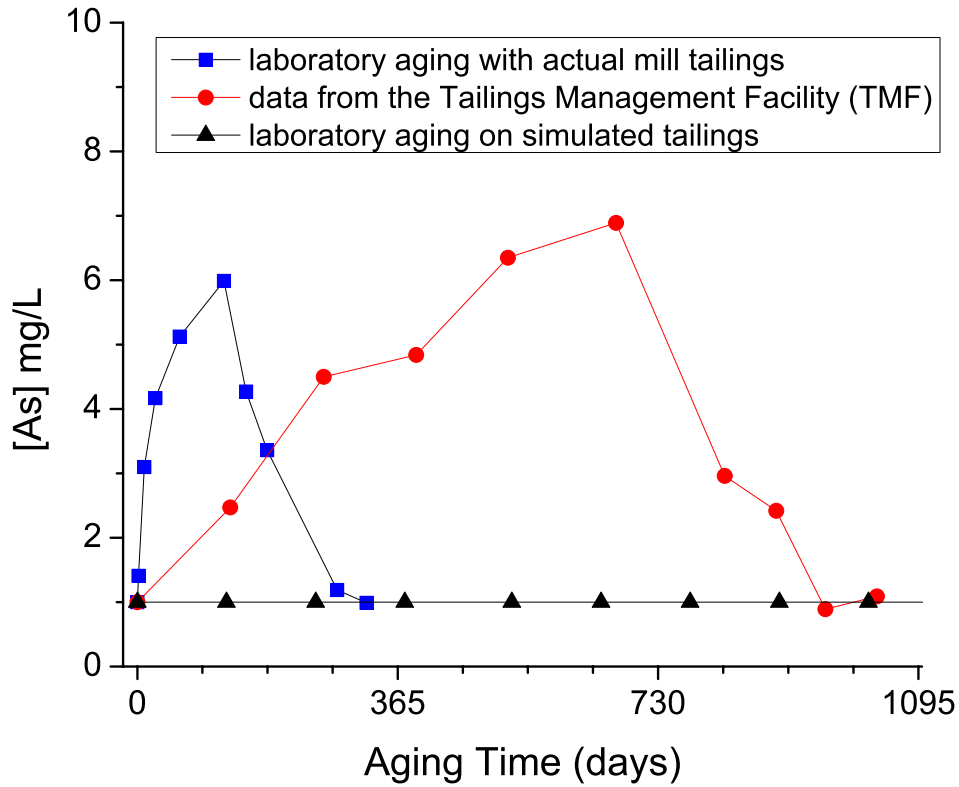
Solid and Solution Speciation

A barge mounted drill rig was used to sample pore waters and to obtain cores of the TMF material.

Arsenic concentrations exhibit a time-dependant rise and fall, peaking at ~7 mg/L after 2 years in the TMF (red curve).

The shape of the curve is similar to laboratory aging of real tailings material (blue curve).

Both curves stabilize after 3 years, at under 1mg/L.



Observed Arsenic aging behaviour on simulated and real tailings material

Solid Speciation using XANES

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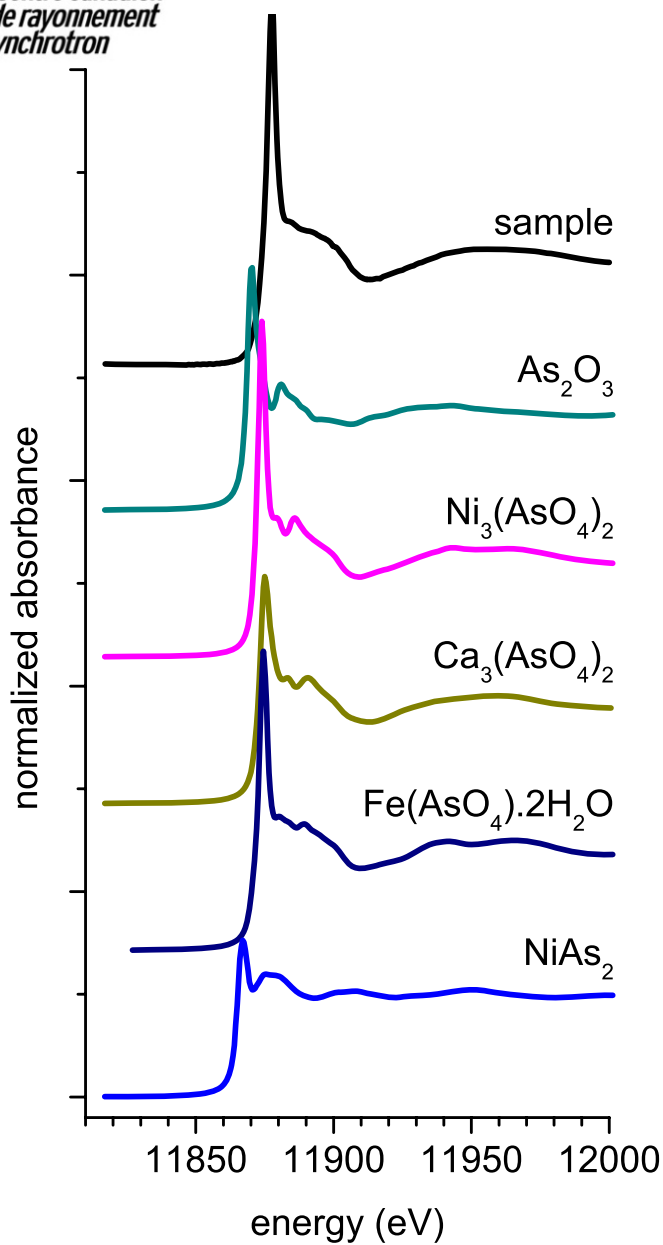
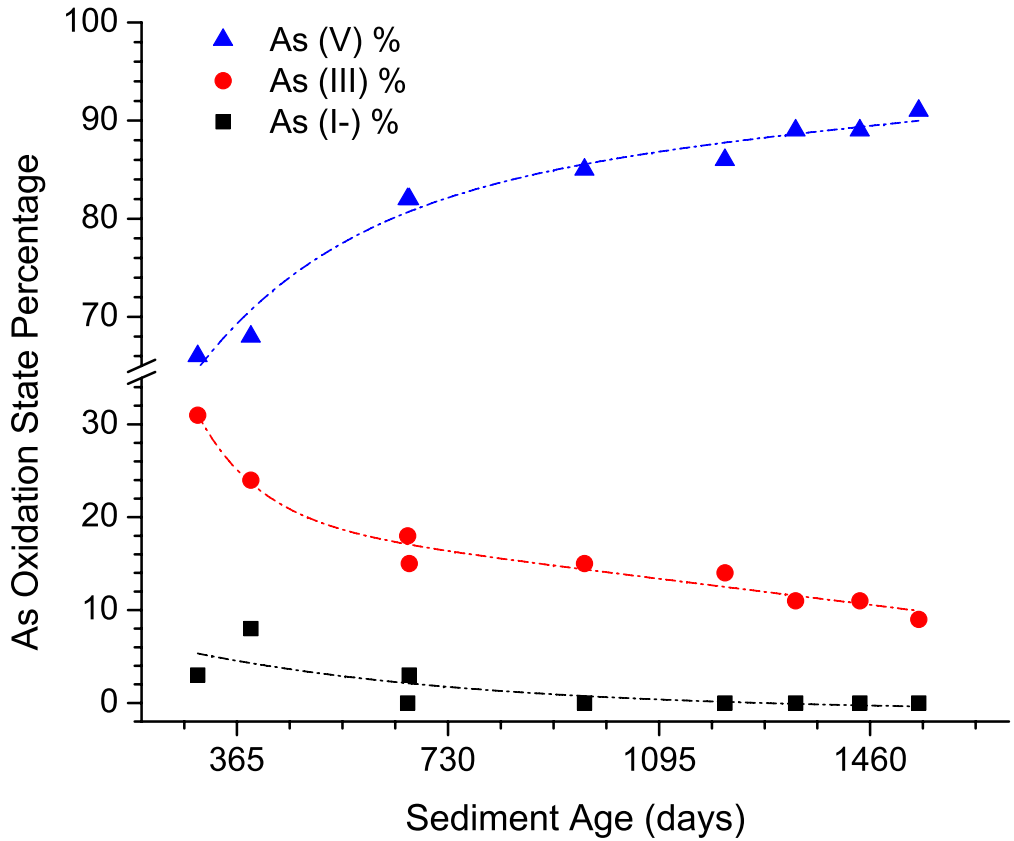


4 years of exposure in the TMF environment clearly show a trend in the solid phase.

Both arsenide and arsenite phases are decreasing with simultaneous increase in the As(V) oxidation state.



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Summary and Conclusions

- Areva Resources is concerned with the long term stability of arsenic in mine tailings after their disposal in the JEB TMF at McClean Lake, SK. The tailings are composed of secondary non-crystalline mineral precipitates.
- In order to predict the evolution of arsenic bearing phases, As K-edge XANES analysis was used to determine the arsenic oxidation state and speciation in core samples and their relative proportions.
- Changes in the arsenic speciation of solid core samples from the TMF and the time-dependant rise and fall of total arsenic in pore waters suggests oxidation of arsenic in pore waters.
- After 4 years in the TMF, trends in the arsenic speciation indicate increasing As(V) species.
- Additional XANES and EXAFS investigations have identified the As(V)-containing mineral to be a poorly crystalline scorodite.


Thanks for your Attention