# Arsenic in Uranium Mine Tailings: XAFS and X-ray Microprobe Studies

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## Introduction

Arsenic contamination within mine tailings is one of the most important environmental issues facing the uranium mining industry. Arsenic is one of the primary contaminants of concern in terms of potential to affect downstream receptors. The long-term stability of arsenic within uranium mine tailings is controlled by such factors as pH, Eh, temperature, as well as the type of arsenic mineral found within the tailings.

Approximately 80% of the arsenic present in the host rock is leached during the acidic leaching stage of uranium. The remaining 20% of the arsenic, in its native form, is found in the minerals niccolite (NiAs) and gersdoffite (NiAsS).[1] These primary minerals representing approximately 20% of the mass of the tailings are unaffected by the milling process and are subsequently discharged to the tailings in their native form.

The mineralogy of the majority of the arsenic found as secondary precipitates within the tailings is of particular interest. The effective determination of the long-term stability of arsenic within uranium mine tailings using geochemical thermodynamic modeling is a futile exercise without the knowledge of the mineralogy of the secondary arsenic precipitates.

The mineralogy of the secondary arsenic precipitates in uranium mine tailings was previously investigated using conventional techniques.[1-3] In these investigations it was suggested that secondary arsenic precipitates can be found in three general mineralogical forms. With sufficient iron present in the milling circuit it was speculated that arsenic, present as the arsenate anion ($AsO_4^{3-}$), precipitated with iron as scorodite ($FeAsO_4 \cdot 2H_2O$).[2] Arsenic concentrations in the tailings pore water should not be expected to exceed 0.1 mg/l when arsenic was precipitated as scorodite.

It was suggested that arsenic was released from scorodite (formed at pH <4) in the milling process as the pH of the tailings slurry was increased past 7. This resulted in the adsorption of arsenic to hydrous ferric oxide (HFO).[3] Several XAFS studies to investigate the nature of arsenic adsorption to hydrous ferric oxides have been carried out.[4-6]

Under conditions encountered when there was a lack of iron in the uranium milling circuit, secondary calcium arsenates were speculated to have precipitated in the milling circuit.[1,3] The mineralogy of secondary calcium arsenates is also very important to the understanding of the long-term stability of arsenic within the tailings. It was found that several secondary calcium arsenate precipitates could be formed based on milling conditions. The different calcium arsenate minerals exhibit a wide range of thermodynamic solubility within the tailings.[7] Quantitative arsenic speciation using x-ray absorption spectroscopy has previously been conducted on gold mine tailings in California.[8] In the study it was concluded that EXAFS analysis of mine tailings containing several mineralogical species of arsenic was very complicated.

In this study we have used both XAFS and microprobe fluorescence imaging to study the uranium mine tailings at various stages of the tailings production, aiming to have a better understanding of the mineralogical structure of the secondary arsenic minerals.

## Methods and Materials

PNC-CAT beamline 20-BM was used to obtain As K-edge XAFS on a series of tailings samples from Rabbit Lake storage pit (SK, Canada) and fresh tailings (neutralized raffinates, precipitate from liquid tailings). Synthetic ferric arsenate ($FeAsO_4$, scorodite) prepared by Dr. G. Demopoulos at McGill University and two arsenates absorbed on FeOOH mineral[3] were measured as XAFS reference compounds. Fluorescence ionization chambers were used to measure XAFS in fluorescence mode, except for the scorodite reference, which was measured in transmission mode. An Au foil was in the transmitted beam path after the sample to provide the Si(111) double-crystal monochromator energy calibration, which agrees well with the internal goniometer encoder calibrations. Beamline 20-ID equipped with a Kirkpatrick-Baez mirror system was used to obtain 5 μm resolution (As, Fe, Ni, Ca) fluorescence yield images over several areas of 0.5 mm in diameter. Fluorescence signal was detected using a 13-element Ge detector. Scanning electron microprobe (SEM) spectroscopy has shown previously that arsenic-containing grains are in the range of 50 to 100 μm in diameter.[3] Using the microbeam from 20-ID, As K-edge XAFS data from selected single As-containing grains were also obtained.
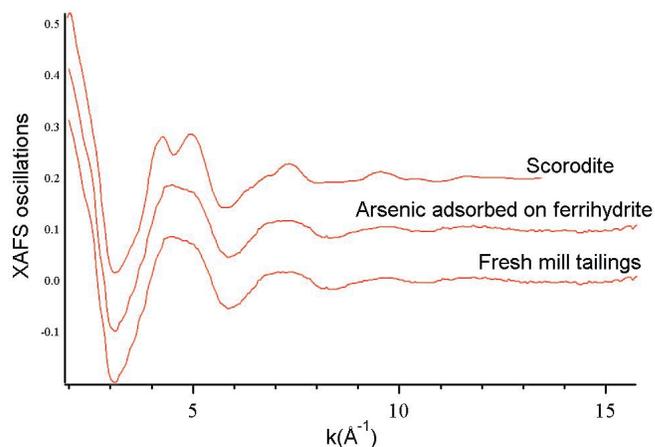


FIG. 1. Comparison of As K-edge c(k) of a crystalline scorodite, arsenate adsorbed on FeOOH and fresh mill tailings.

## Results

Figure 1 shows a comparison between $\chi(k)$ of a fresh mill tailings (neutralized raffinate, Fe/As = 4) and those from refer-
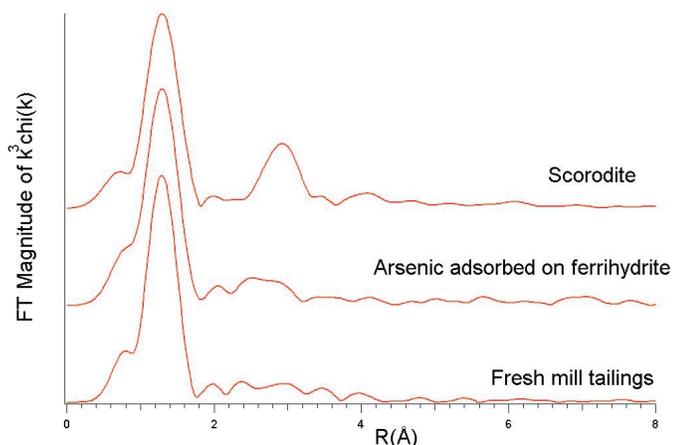
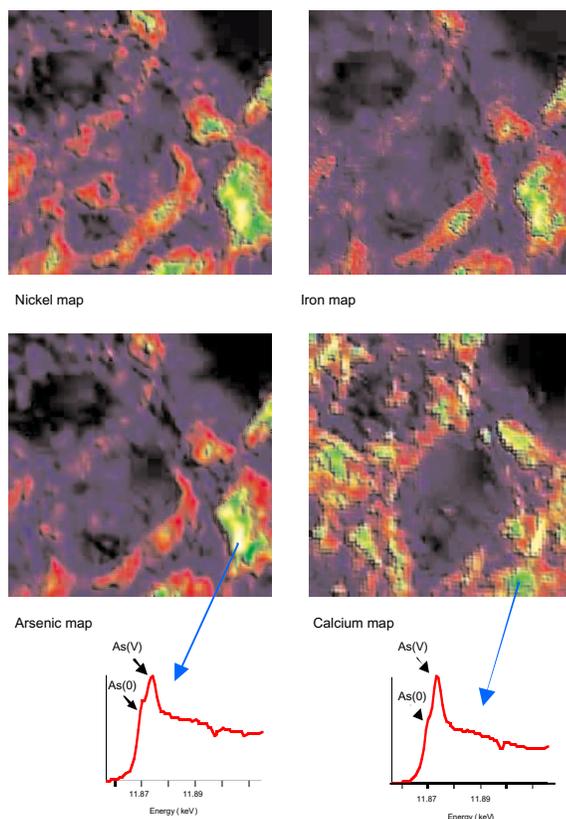FIG. 2. Comparison of the Fourier transform magnitudes obtained from data in Fig.1.



FIG. 3 Fluorescence yield images of uranium mine tailings (sample contains fresh mill tailings and leach residuals, i.e. the actual material released into the storage pit). Image area is 500 x 500 mm2 area and with 5 mm beam spot, brighter color indicates higher concentration of the element imaged. Two inserts show the XANES obtained from a Fe-rich and a Ca-rich area, respectively.

ence compounds, scorodite and arsenate absorbed on FeOOH, respectively. A close similarity between the raffinate and arsenate absorbed on FeOOH is observed, while the scorodite data show more crystalline features and a difference compared with the other two in terms of more pronounced higher frequency components (higher atomic shells). These differences are more clearly illustrated in the comparison of Fourier transform (Fig. 2). The first peak below the apparent interatomic distance of 1.5 Å repre-

sents the nearest neighbor As-O shell of an arsenate unit. In the scorodite, the peak near the apparent distance of 3 Å is from an As-Fe shell,[3,5,6,8] its counter part in the arsenate absorbed on FeOOH is characteristically shifted towards a shorter distance and accompanied by an intensity reduction due to the change in multiple scattering paths and additional long-range disorder. Qualitatively, it is rather clear that the fresh tailings also show the characteristic As-Fe shortening, which indicates a similar local structure as that in the arsenate absorbed on FeOOH, More detailed FEFF-based analysis[9] is in progress to determine if a mixture model involving absorbed arsenate on FeOOH and disordered small ferric arsenate crystallites would provide a satisfactory characterization.

Figure 3 shows the fluorescence yield images of As, Fe, Ni and Ca from a higher As concentration tailings sample from the Cameco Rabbit Lake Tailings storage pit in Saskatchewan, Canada. It is shown that As-containing grains are of several ten to approximately a hundred microns in size. The correlation in the distribution of Fe and As is clearly shown; it is rather interesting to notice that the same level of correlation between the distribution of Ni and As also exits. Because of the abundance of Ca in the sample, its association with As is not immediately obvious. Two XANES spectra are shown with arrows linked to the sample location where the data were acquired. From the difference of the As(0) to As(5) branching ration in the two spectra, the chemical inhomogeneous nature of the tailings sample is shown. The As(0) species are likely from the leach residuals, because the XANES of fresh tailings discussed show predominantly As(V) valence.

## Acknowledgments

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