

Transformation of As species in wetlands historically used for mine tailings disposal (Ontario, Canada)

S. BEAUCHEMIN AND J. KWONG

Natural Resources Canada - CANMET, Ottawa, Ontario, Canada (sbeauche@nrcc.gc.ca)

Background

Eighty years of silver mining in the Cobalt area (Ontario, Canada) has resulted in widespread contamination of water courses with As. The objective of this study was to determine the impact of changes in redox conditions on the stability of As in wetlands historically contaminated by mine tailings.

Methods

Under controlled laboratory conditions, tailings sampled from a wetland (~1300 mg As kg⁻¹ sediment; pH 7.4) were subjected to a 30-day reduction during which dissolved metal concentrations were monitored. The reoxidation of the samples was then accomplished by air-drying. As oxidation state in the original, reduced and reoxidized tailings samples was determined using X-ray absorption spectroscopy (XAS).

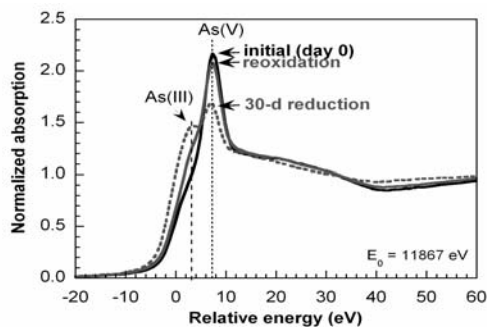


Figure 1. As K-XANES spectra for tailings subjected to 30-day reduction followed by reoxidation.

Results and Discussion

XAS analyses confirm that changes in As speciation readily occur with changes in redox conditions in the tailings sediments, resulting in rapid mobilization of As. These results will be discussed in the light of other field data suggestive of microbial sulfate reduction occurring locally in the wetland with probable co-precipitation of arsenic as a sulfide associated with framboidal pyrite.

Conclusion

This study clarifies the transformation and mobilization of As in a typical wetland area in the historic Cobalt mining camp characterized by elevated dissolved As in near-neutral drainage. The results elucidate the impact of the tailings disposal scenario on the deterioration of water quality.

Molecular speciation, mineral residence, and geochemical behavior of U in contaminated subsurface sediments

JOHN M. ZACHARA¹, JIM MCKINLEY¹,
CHONGXUAN LIU¹, ZHEMING WANG¹, JEFF CATALANO²,
GORDON BROWN³ AND NIK QAFOKU¹

¹Pacific Northwest National Laboratory, Richland, WA 99352, USA

²Argonne National Laboratory, Argonne, IL 60439, USA

³Stanford University, Stanford, CA 94305, USA

Uranium is an important geochemical element that exhibits complex chemistry. In the hexavalent state, it is a serious groundwater contaminant at sites of U-mining/milling and nuclear materials processing. We have investigated U-contaminated sediments from different vadose and saturated zone plumes at the U.S. DOE Hanford site with the objective to develop a generalized geochemical model of U for this semiarid, mildly calcareous geochemical regime.

We describe results of spectroscopic (XAS, CLIFS, synchrotron diffraction) and microscopic (TEM, SEM, EMP, XMP) measurements to define the chemical form and spatial distribution of contaminant U(VI). Multiple techniques were required for definitive identification because of ambiguous spectroscopic signatures. A complex continuum was found between adsorption and precipitation. At one location U(VI) was found as micron-sized intragrain uranyl silicate precipitates in mm-sized granitic lithic fragments that comprised a small fraction of the sediment mass. At another location, spectroscopic measurements implied that sorbed U(VI) was present as a coprecipitate within waste-derived calcite. Deeper in this same plume, sorbed U(VI) was found within micron-thick grain coatings that were enriched with Cu(II) in the form of malachite. Batch and column desorption/dissolution experiments with these materials displayed strong and complex kinetic behavior regulated by microscopic physical and chemical factors. With the exception of the sediments containing uranyl silicates, steady state water compositions rarely conformed to the solubility of known U(VI) phases. Long-inground residence times (30-50y) have allowed significant intragrain diffusion and the formation of stable phase associations.