

***In-situ* metal speciation in soils using synchrotron based techniques**

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INTRODUCTION

Contamination of the environment resulting from anthropogenic activities such as mining, smelting and agriculture is of great public and political concern. As such, a greater understanding of the mobility, bioavailability and long-term fate of the materials resulting from these activities is needed in order to make more accurate decisions when devising remediation and legislative strategies. To provide an accurate description of the fate of metal contaminants in heterogeneous systems, it is essential to understand their speciation. Macroscopic chemical analyses are not sufficient and hence must be complemented with advanced molecular scale techniques. Synchrotron based micro x-ray fluorescence and extended x-ray absorption (μ -SXRF, μ -EXAS) spectroscopies provide the needed selectivity by allowing one to probe, *in-situ*, the local coordination environment of a species over a wide range of concentrations in homogeneous and heterogeneous environments. The resultant structural information provides a mechanistic understanding of the processes controlling the fate of contaminants under environmentally relevant conditions. Current research conducted at the ALS by our group has focused on the application of μ -EXAS and μ -SXRF techniques at beamline 10.3.2 to investigate the speciation of zinc (Zn), nickel (Ni), and arsenic (As) in contaminated soils.

CHANGING ZINC SPECIATION IN A REMEDIATED SMELTER SOIL

Zinc is an essential trace element in plants; however, at higher available concentrations it can become phytotoxic. In the topsoil around former Zn smelters and on sewage sludge sites, weight percent levels of Zn can be present often leaving little or no vegetative cover. *In situ* remediation (immobilization/ inactivation) of these large contaminated sites using soil amendments, which modify the physicochemical properties of the contaminating heavy metals, is a valuable alternative for more expensive and complicated civil engineering techniques, i.e. excavation and landfilling of the contaminated soil. Regulatory acceptance of *in situ* immobilization as a secure reclamation method depends on the ability to predict the long-term stability of such remedial treatments. As such, we probed the changes in Zn speciation resulting from reclamation procedures in an effort to predict the long-term stability of the metal. Soils were obtained from a former zinc smelter (Belgium), where 135 ha of land were heavily contaminated. Three hectares of soil were successfully remediated by adding beringite (an aluminosilicate by-product from coal burning) and compost to the soil. Twelve years after remediation, healthy vegetation has developed on this site.

Zinc speciation was accomplished by a combination of μ -focussed XAS spectroscopy, principal component analysis and linear combination fitting of Zn k-edge spectra for treated (12yrs) and non-treated soils.

Preliminary results indicate that in both the treated and non-treated soils, Zn is mainly present in franklinite and willemite, the two primary Zn ore minerals that were refined at this site. In both soils, significant amounts of Zn were incorporated into Zn-Al layered double hydroxides (Zn-Al LDH). These Zn-Al LDHs form under non acidic conditions at the surfaces of aluminosilicates and likely play an important role in decreasing metal bio-availability. In the non-treated soil, a small fraction of Zn was found sorbed to birnessite and ferrihydrite. In the treated soil, this sorbed fraction was mainly absent and a small Zn fraction was incorporated into the beringite mineral. Micro-focussed XAS spectroscopy greatly enabled us to distinguish the small differences in Zn speciation between the treated and non-treated soils. These small variations are likely responsible for the differential toxicity between the treated and non-treated soils.

NI SPECIATION IN REFINERY SOILS

Several hundred hectares of farmland were rendered unsuitable for crop production due to nickel (Ni) emissions from a nearby refinery. Nickel concentrations away from the refinery decrease, while soil pH increases. In order to predict the mobility, solubility and bioavailability of Ni, a mineral soil adjacent, intermediate and about 3 km away from the refinery were investigated to determine the effects of pH, distance (i.e., particle size) and Ni concentration on metal phase associations.

Initial results indicate that nickel is dominantly in the form of NiO in soils closer to the refinery with a pH regime between 5.9 and 6.6. In the soils farthest from the refinery (~3 Km) and with neutral pH, disordered nickel hydroxides predominate. Interestingly, soil samples which were collected from intermediate locations, contained significant fractions of both nickel oxide and the disordered hydroxide.

Initial μ -SXRF analyses of these soils revealed little association of Ni with neither the mineral and organic phases in the soils, nor was it co-precipitated with other metals. Although the associations of Ni with any of the soil components are not evident in the current studies, they cannot be completely

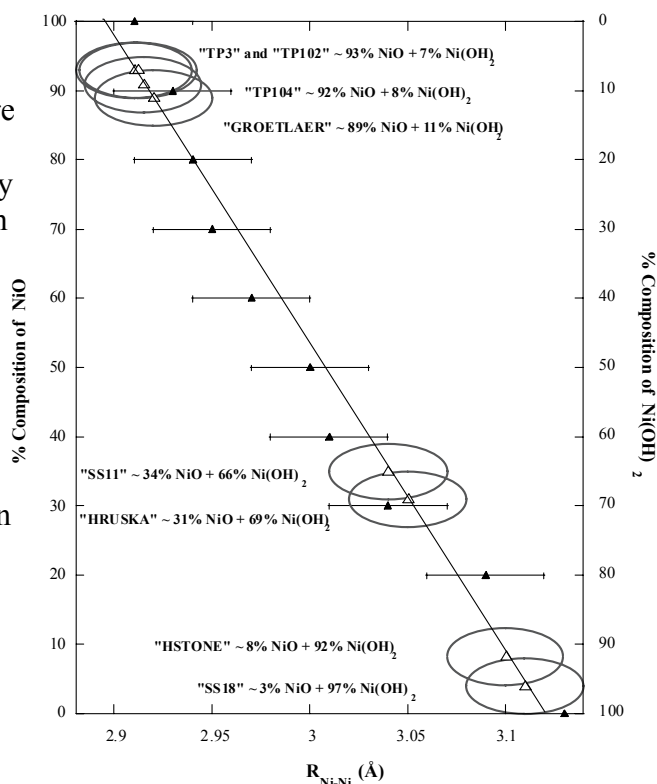


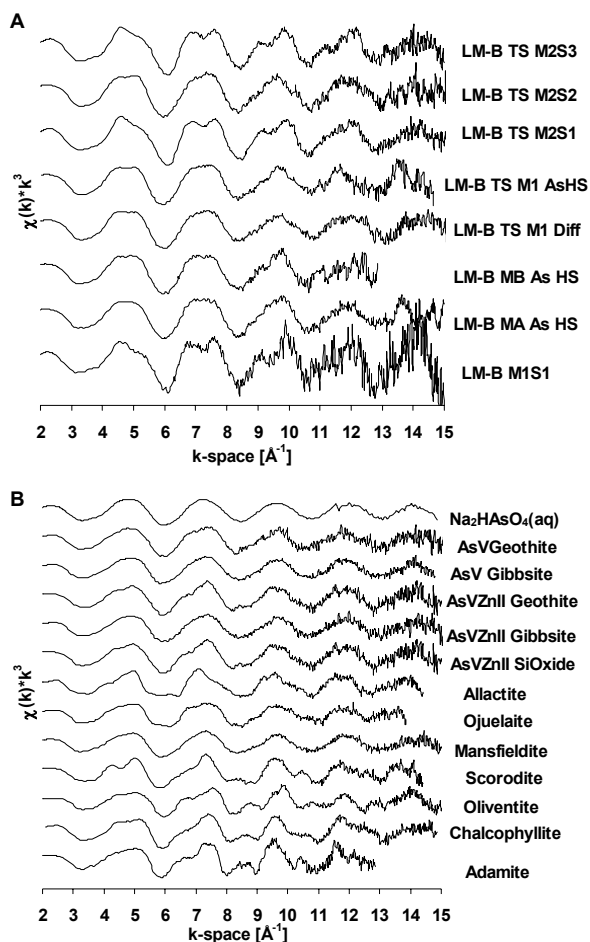
Figure 1: The linear combination model (LCM) correlating the Ni-Ni bond distance and the weight % composition of NiO in NiO + Ni(OH)₂ mixtures. The R_{Ni-Ni} results from the Ni k-edge XAS analyses of the mixtures (solid triangles) and the contaminated soils (open triangles). LCM is: (% NiO) = $1382.3 - 443.06 \times R_{Ni-Ni}$; $r^2 = 0.96$

ruled out, since it is likely that the signals from the high NiO concentrations swamp the signals arising from the sorption complexes. However, for these samples, both the bulk XAS and micro-XAS analyses confirmed that Ni predominantly exists as oxide or hydroxide species. As a result, linear combination analyses were constrained to estimate the relative concentrations of NiO and Ni(OH)₂ in the soil samples. The linear combination analyses (Figure 1) suggest that 90-95% of the Ni in the samples closer to the refinery (TP3, TP102, TP104 GRTL) is present as NiO. On the other hand, Ni(OH)₂ comprises nearly 92-97% of the Ni in the samples farthest from the refinery (HSTONE, SS18). In addition, the intermediate soil samples (SS11 and HRUSKA) contained approximately 30-35% NiO.

ARSENIC IMPACTED SOILS

Our arsenic (As) research has focused on identifying the solid phase speciation of arsenic in a sandy loam soil contaminated with copper chromated arsenate (CCA) and zinc. As part of the site's remediation process, the pH was raised to 7; operations at the site ceased ca. 50 years ago. The presence of different metals allows us to investigate the effect(s) these metals may have on arsenic solid phase speciation.

Previous investigations revealed that arsenate (As(V)) was the dominant oxidation state in this soil and μ -SXRF maps identified significant spatial co-occurrence between As (V) and zinc, and As (V) and copper in both the upper and lower soil layers. Arsenate appears both as precipitates and adsorption complexes in the soil. In the top layer (0-20cm), mostly As (V) adsorption complexes are observed (data not shown). With increasing depth (20-40cm), As (V) appears to occur both as precipitates and adsorption complexes (Panel A). In comparison to mineral and sorption standards (Panel B), these precipitates show similarities to olivenite, chalcophyllite, and adamite suggesting that copper-arsenates and possible mixed zinc-copper arsenates phases exist. A possible factor of formation in the lower rather than the upper soil layer is the smaller fraction of natural organic matter competing for metal complexation.



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