

A microspectroscopic study on the influence of the inherent heterogeneity of waste repository materials on contaminant uptake

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Large-scale problems such as toxic metal environmental disturbance and nuclear waste remediation and storage are now recognized to be interconnected to small scale-mechanisms. In this study we have combined micro X-ray fluorescence (XRF), micro X-ray absorption spectroscopy (XAS) with 'bulk' XAS to gain spatially resolved information on the speciation and structural coordination environment of contaminants solidified in cement. Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of radioactive wastes in underground repositories. From a chemical standpoint, cement is a complex heterogeneous mixture (calcium (aluminium) silicate hydrates, Ca(OH)₂, calcium aluminates, and some highly reactive minor phases) with discrete particles typically in the size range of a few to a few hundred micrometers.

An example addressing the heterogeneity of sorbent cement concerns the microbial influenced degradation of a cobalt-containing cement matrix. Since microorganisms can affect the chemical speciation of contaminants in a cementitious environment, the cobalt-containing cement material was analyzed by a set of analytical techniques before and after extended microbial degradation by chemotrophic bacteria (*Thiobacillus thiooxidans*) that were colonized on the waste material. Despite serious precautions to achieve a homogeneous cement paste prior to solidification, the distribution of Co in the final solid waste product is characterized by a considerable degree of spatial heterogeneity. Simultaneously, distinct Co-free 'islands' and Co-rich 'hot spots' are observed. Most of these features have a characteristic length-scale that is in the order of a few micrometers. With increasing magnification, some of these hot spots have been identified as *grain coatings* while others turned out to be distinct *Co-rich precipitates*. XAS investigations on the unaltered part of the cement matrix and the corrosion zone revealed noticeable differences in the EXAFS and data analysis indicate that the redox conditions and Co speciation in the bulk matrix of the cement paste differs from those in the corrosion zone and the corrosion front. This finding demonstrates the importance of small-scale mechanisms and molecular-level processes in complex heterogeneous systems and illustrates the increasing need for the realization of synchrotron-based high resolution analytical X-ray probes.

Spatial and temporal variation of Zn species in the rhizosphere of a contaminated soil

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Contamination of soils with Zn from anthropogenic sources is an increasing problem in industrialized countries, potentially impeding the production of food and fiber. The effective, short-term effect of Zn depends on the amount and the chemical nature of the most mobile species, while the long-term ecotoxicity is determined by the resupply of the mobile pool from more stable phases. Thus, quantitative speciation as well as its variation with time is a prerequisite for long-term risk assessments.

Due to the heterogeneous distribution of water, minerals organic matter and biota, diverse chemical microenvironments may coexist on micrometer to millimeter scales, leading to gradients in Zn speciation. Especially in the rhizosphere where roots alter, e.g., pH, redox, and the concentration of organic chelators, Zn speciation may significantly deviate from that in bulk soil. Therefore, we investigated the Zn speciation after mixing a soil with dust particles emitted by a metal foundry, using bulk X-ray absorption fine structure (XAFS) spectroscopy and selective sequential extractions (SSE) to follow the temporal variation, and using micro X-ray fluorescence (μ -XRF) and μ -XAFS spectroscopies (5 μ m spatial resolution) to follow the spatial variation in the rhizosphere soil.

The dust particles consisted predominately of zincite (ZnO), which dissolved in the soil within 7 d (water saturated) or 6 months (unsaturated). After dissolution, the predominant part of Zn was bound as inner-sphere sorption complex. The figure below shows the Zn distribution within a 1.5 x 1.5 mm² large area around a root (delineated by hatched lines). A Zn plume extends from a dissolving zincite particle towards the root and Mn- and Fe-rich zones. Micro-XAFS suggested that the dominant Zn species after 3 months is tetrahedrally coordinated Zn sorbed to root tissue and to Mn- and Fe-oxides.

