

2.3.P09**A new *in situ* method to follow reactions of minerals under environmental conditions**A. BIRKEFELD¹, B. NOWACK² AND R. SCHULIN³¹ ITOe, ETH Zürich, Grabenstr. 3, CH-8952 Schlieren (birkefeld@env.ethz.ch)² ITOe, ETH Zürich, Grabenstr. 3, CH-8952 Schlieren (nowack@env.ethz.ch)³ ITOe, ETH Zürich, Grabenstr. 3, CH-8952 Schlieren (schulini@env.ethz.ch)**Introduction**

To assess the risk potential of metal contamination in soils it is important to know the behaviour of particulate contaminants which entered the soil. Examples of such particles are heavy metal containing dusts or metalliferous minerals like ores particles from anthropogenic sources. The long-term dissolution behaviour and phase transformations of these mineral particles determine their environmental risk potential.

Method and materials

We will present a new in-situ method to investigate the behaviour of particles like heavy metal minerals under environmental conditions in soils or sediments. Polymethylmethacrylate (PMMA) polymer supports were coated with selected heavy metal minerals on a thin epoxy resin film. This method provides direct contact of the particle surface with its surrounding matrix (soil, sediment) and enables an easy recovery. The polymer supports were inserted into different soils under environmental and laboratory conditions. After different time periods they were recovered and analyzed for phase transformations and dissolution features.

Results and outlook

Scanning electron microscopic (SEM) photographs, x-ray probe spectra and Raman spectroscopy showed clearly the occurrence of newly formed mineral phases in some mineral/soil combinations. Dissolution of minerals is characterized by quantifying the remaining metals. First results showed that this new method is an easy tool to obtain information on the reactions of particles in soils. The method has the potential to be used in other systems such as sediments or aquatic environments.

2.3.P10**Wet chemistry and TRLFS studies of Eu(III) and Cm(III) uptake by cementitious materials**E. WIELAND¹, T. STUMPF², J. TITS¹ AND T. FANGHÄNEL²¹ Paul Scherrer Institut, Waste Management, CH-5232 Villigen PSI, Switzerland (erich.wieland@psi.ch)² Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung, D-76021 Karlsruhe, Germany

Knowledge of immobilisation mechanisms on a molecular scale is a prerequisite for predicting the mobility and long-term fate of hazardous contaminants and radionuclides stabilized in cementitious matrices. This has led to an increase in research using spectroscopic and micro-spectroscopic techniques for investigating uptake mechanisms of heavy metals and metalloid ions at the solid/liquid interface of cement minerals and in the complex cement matrix.

In the present study, the Eu(III) and Cm(III) uptake by hardened cement paste (HCP) and calcium silicate hydrates (C-S-H) phases has been investigated using macroscopic (batch sorption experiments) and spectroscopic (Time-Resolved Laser Fluorescence Spectroscopy (TRLFS)) techniques. Eu(III) and Cm(III) are considered to be chemical analogues for Am(III), which is an important trivalent actinide in nuclear wastes. C-S-H phases (CaO, SiO₂, xH₂O) are the main constituent of "fresh" and degraded HCP (~ 40-60 wt.%) with a large capacity for ion uptake. Wet chemistry studies with Eu(III) were undertaken to determine uptake kinetics and sorption isotherms on HCP and C-S-H. The coordination of Cm(III) in these solid materials was probed using TRLFS.

The macroscopic studies show that the distribution ratio (R_d) for Eu(III) on HCP and C-S-H are very high (typically $> 10^2 \text{ m}^3 \text{ kg}^{-1}$). Sorption on these solids is linear up to a maximum solution concentration of about 10^{-6} M . TRLFS measurements reveal the formation of four different Cm(III) species in the Cm(III)/HCP system: A non-fluorescing species, which corresponds to colloidal Cm(III) hydroxide, a fluorescing Cm(III) species sorbed onto portlandite, which is an important constituent of the cement matrix (~20-25 wt.%), and two fluorescing Cm(III) species associated with C-S-H. Analysis of the fluorescence emission lifetimes further shows that the two fluorescing Cm(III)/C-S-H species have one to two and no water molecules, respectively, left in their coordination spheres. This can be rationalized as Cm(III) being incorporated into the C-S-H structure. Based on the above findings a model for Cm(III) uptake by HCP and C-S-H is proposed: one Cm(III) species substitutes for Ca(II) in the interlayer of C-S-H, and the other one replaces Ca(II) in the octahedral layer of C-S-H. The TRLFS study provides direct evidence that Cm(III), and presumably other trivalent actinides and lanthanides, are incorporated into the C-S-H structure of the complex cement matrix.