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Micro-scale Chemical Speciation of Highly Heterogeneous Cementitious Materials Using Synchrotron-based X-Ray Absorption Spectroscopy

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Mixing 'fugitive' hazardous waste products into a cementitious binder system improves the stabilization and the solidification of radioactive and industrial waste materials. Consequently, the migration of radionuclides and other heavy metals from cement-based landfills and nuclear underground waste repositories into the environment can be significantly retarded and possible impacts on the environmental quality can be minimized. From a chemical standpoint cement minerals are typically present as discrete particles in the size range of a few nanometers to a few hundred micrometers (Fig. 1). The complexity of the hydrated assemblage and the reactivity of the minerals make it very difficult to investigate cementitious systems.

Molecular-level investigations on Co(II) doped hardened cement paste were carried out at the Advanced Light Source (ALS) using synchrotron-based micro-X-ray fluorescence (XRF) and micro-X-ray absorption spectroscopy (XAS). XAS is exclusive to synchrotron light sources and can yield spatially-resolved information (*e.g.* type of neighboring atoms, bond length and coordination numbers) on the variability of chemical speciation in complex and highly heterogeneous samples. A hard X-ray micro-probe facility optimized for micro-XRF and micro-XAS with a spatial resolution of a few μm^2 has now also become available at the Swiss Light Source (SLS).

The micro-XRF maps show that Co is heterogeneously distributed in the Co-doped cement matrix (Fig. 2). Typically Co-rich spots up to ~50 μm^2 in size (*e.g.* spot 1) as well as characteristic Co-rich ring-like structures with diameters up to ~200 µm (*e.g.* spot 2) were observed. XAS data analysis revealed the presence of a Co(II)-hydroxide-like phase ($Co(OH)_2$ and/or Co-Al layered double hydroxide) at spot 1 and a Co(III)OOH-like phase at spot 2. This finding is illustrated by the shorter Co–O and Co–Co distances at spot 2 (Fig. 3).

Co oxidation is environmentally relevant since it results in a reduction of the Co mobility in cement. A surprising result of the micro-spectroscopic study is that oxidation of Co(II) is a locally occurring process. ***This finding demonstrates that the inherent micro-scale heterogeneity of cement may well control the overall chemical reactivity of Co in cement.***

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References

Website of the microXAS at SLS: *http://sls.web.psi.ch/view.php/beamlines/mxas/index.html*.

M. Vespa, R. Dähn, D. Grolimund, M. Harfouche, E. Wieland, A.M. Scheidegger, *J. Geochem. Exploration* **2006**, in press.

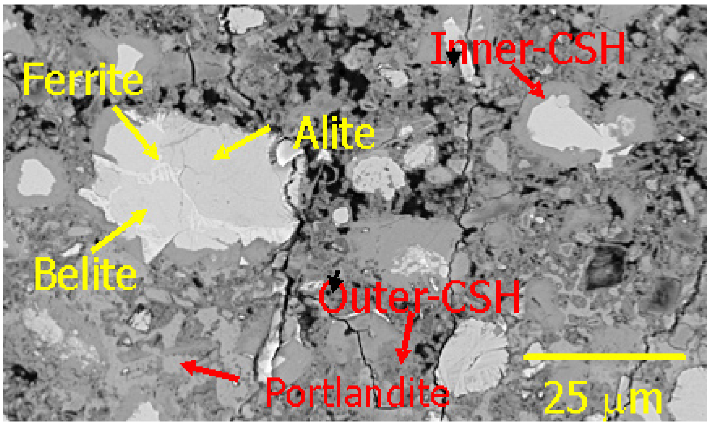

Fig. 1. SEM image illustrating the micro-scale heterogeneity of hardened cement paste. Examples of clinker minerals (ferrite, belite and alite; yellow) and hydrated phases (calcium silicate hydrates (CSH) and portlandite; red) are outlined.

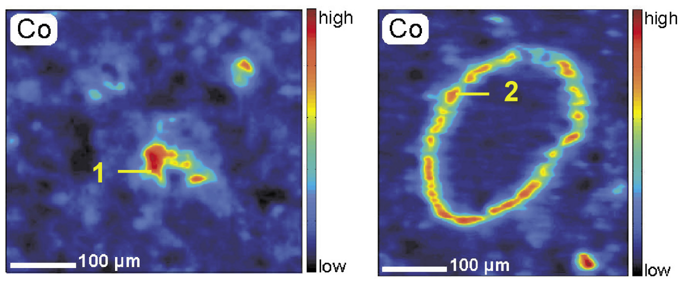

Fig. 2. Micro-XRF maps showing the elemental Co distribution in a hydrated Co-doped hardened cement paste at different locations (beam size ~ 5x5 μm^2)

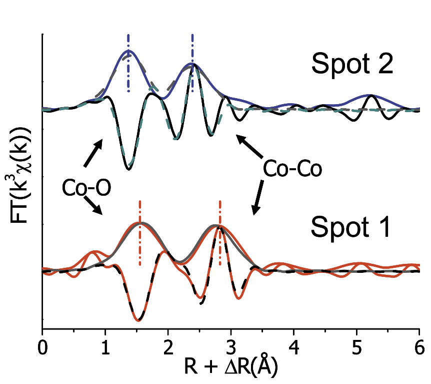

Fig. 3. Experimental (solid line) and theoretical (dashed line) Fourier transforms (modulus and imaginary parts) of k^3-weighted micro-EXAFS spectra collected at spot 1 and 2. The spectra are uncorrected for phase shift (R + ΔR).