

## 4.2.34

### Metal speciation in heterogeneous waste repository materials using micro-XRF and micro-XAS

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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. For example, in the past much of our understanding of uptake processes of contaminants at the solid-liquid interface has been obtained by resorting to 'bulk' analytical techniques and wet chemical laboratory experiments. In certain cases such methodology may be sufficient to yield molecular-level information on fate of contaminants in natural and man-made materials, but the approach breaks down when mechanisms operative on the micro-scale have larger consequences.

In this study we have combined synchrotron-based micro X-ray fluorescence (micro-SXRF), micro X-ray absorption spectroscopy (micro-XAS) with 'bulk' XAS to gain spatially resolved information on the speciation and structural coordination environment of contaminants (Co, Ni) in cement, a complex heterogeneous mixture with discrete particles typically in the size range of a few to a few hundred micrometers. Overall, the material mainly consists of calcium (aluminium) silicate hydrates, Ca(OH)<sub>2</sub>, and calcium aluminates, but includes also some highly reactive minor phases such as Fe-hydr(oxides), Mn oxides, and phosphates minerals.

Another example addresses the corrosion of iron waste canisters used in waste management. Under anoxic conditions zero-valent iron can react with water to produce a thin green rust layer that is highly reactive towards reduction processes of radionuclides. For example, micro-SXRF and micro-XAS investigations revealed that the selenium immobilization in the presence of Fe(0) was accompanied by the formation of a Se-rich few µm-thick green rust corrosion layer in which the selenium was present in a reduced form. These findings suggest that the reactivity of zero-valent iron and green rust should be considered in assessing the long-term fate of selenium in waste repositories.

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### Fate of molybdate in the sea; Insights from the laboratory

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Black shales and modern euxinic marine sediments contain elevated Mo concentrations, which convey information about redox conditions during deposition. Optimal use of this information necessitates a better understanding of Mo capture mechanisms. A key control on Mo behavior is the activity of molecular H<sub>2</sub>S (aq), which must reach ~10<sup>-5</sup> M before the geochemically inert MoO<sub>4</sub><sup>2-</sup> in seawater will begin to convert to particle-reactive thiomolybdates (MoO<sub>x</sub>S<sub>4-x</sub><sup>2-</sup>, x = 0-3) [1]. This conversion requires years or decades in homogeneous seawater, but is catalyzed by mineral surfaces [2]. Surface catalysis may explain why Mo scavenging from anoxic marine waters occurs more often within sediment pore waters, rather than in overlying waters. When H<sub>2</sub>S is below the critical threshold, Fe monosulfides are able to scavenge Mo weakly, but this form of Mo is not geologically robust; scavenging is reversed by even brief O<sub>2</sub> penetration episodes. Pyrite is relatively refractory during O<sub>2</sub> penetration episodes. Pyrite is an important host-phase for Mo in both euxinic sediments and black shales. Mo is captured irreversibly by pyrite surfaces as Fe-Mo-S cluster complexes. These complexes may survive for >10<sup>8</sup> y in black shales [3]. The reaction pathway leading to these products requires Mo<sup>VI</sup> reduction [4], which is accomplished by S<sup>0</sup>-donors (mainly polysulfides) through an unusual, ligand-induced electron transfer process [5]. Polysulfides not only convert Mo to forms suitable for scavenging by pyrite, but promote pyrite growth as well. This proposed mechanism of Mo scavenging by pyrite can operate over a broad redox range. No critical pE threshold for Mo scavenging can be specified other than that conditions sufficient for biological sulfate reduction must exist [5]. Polysulfide-activated Mo may also account for organic-bound forms of Mo in sediments, but this aspect of Mo fixation remains to be investigated in detail.

#### References

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