



Experiment title: In situ measurement of radionuclide speciation in concrete	Experiment number: EV-174
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Background

Reinforced cementitious structures in nuclear waste repositories are widely spread. Adsorption and redox reactions of radionuclides (RNs) on these structures are critical processes to safety assessment of repositories. Recently, we have studied RNs sorption behaviors on a minor phase present in hydrated cement, alumina ferric oxide monosulfate (so-called AFm) phase $[\text{Ca}_4\text{Al}_2(\text{OH})_{12}]^{2+} \cdot \text{SO}_4^{2-} \cdot m\text{H}_2\text{O}$, which is considered to be potential scavengers of soluble RN anions, via both surface adsorption and anion exchange processes^[1]. In concrete, pH is always maintained at ~13 due to the cement hydration, while the interfacial Eh is still undetermined so far and largely controlled by the steel corrosion (a thin film over a few micron), ordinarily described by a “sandwich” $\text{Fe}^{\text{II}}(\text{OH})_2/\text{Fe}_3\text{O}_4/\text{Fe}^{\text{III}}(\text{OH})_3$ (from inner to outer layers) model. Besides, once steel reinforcements (Fe^0) react with groundwater, it should impose the redox potential corresponding to the $\text{H}_2\text{O}(\text{l})/\text{H}_2(\text{g})$ limit and the redox-sensitive RNs released from the cracked container would be reductively precipitated as insoluble phases. However, $\text{H}_2(\text{g})$ is not likely to be reactive without specific catalysis and the $\text{Fe}^0/\text{H}_2\text{O}$ contact be hindered by corrosion passivation products. These iron species (e.g., white rust ($\text{Fe}(\text{OH})_2$), magnetite, goethite, ferrihydrite, hematite, etc.) tend furthermore to impose a more complex Eh potential in cement hydrates. Since local redox potential is a key factor controlling RNs redox reactions and mobility, it is a critical parameter for assessing the risks of a nuclear waste repository. The objective of our experiment on BM25A was to determine the in-situ Eh values predominating within corrugated concrete pore water, by equilibration of synthesized steel corrosion products (e.g., magnetite, hematite, and goethite) with RNs dissolved in cement pore water, and then investigating the control exerted by reactive Fe on RN speciation. A variety of redox sensitive RNs (U, Se, Mo, Sb) have been tested, and their reduced and oxidized species fractions obtained by XANES spectroscopy. Based on concentration distributions of a given RN redox couple in cement pore water and steel corrosion products, the experimental Eh values has been determined.

Experiment

Sorption products of 4 RNs on 5 types of Fe-couples were studied. Approximately, 80 samples (including references) were measured by XANES at four X-ray energies, including 12.6 keV (Se K-edge), 17.1 keV (U L-edge), 20.0 keV (Mo K-edge), and 30.5 keV (Sb K-

edge). Prior measurements, solids were collected, dried, and double-side sealed by kapton tape under anaerobic condition. All samples were measured in fluorescence mode, and N₂ gas purging was used during measurements to avoid oxidation. XANES were acquired and LCF data analysis was performed with ATHENA to obtain the relative proportion of each species.

Results

As seen in Figure 1, high quality XANES data were obtained, and provided information about the oxidation states and adsorption form of Se and Sb sorption products in Fe oxides. LCF data analysis indicate that Se(IV) and Sb(V) can be reduced by NZVI and magnetite into lower valent species. Besides, co-precipitation with Ca was observed in the case of Sb(V) and U(VI). Eventually, the relative percentage of each species in solids was obtained by LCF, facilitating the “in-situ” experimental Eh calculations. The experimental Eh values were found to be somewhat different from the Eh values imposed by corrosion products of steel at the steel/concrete interface. In contrast, the experimental Eh values obtained for a given solid with the various RNs were very consistent. Comparing both, we concluded that, the true Fe-hydroxides couples imposing the Eh redox potential within cement pore water is that of the Fe(OH)₃/ (Fe_xCa_{1-x})(OH)₂ couple. The later solid phase need however to be identified at local interesting spots “in-situ”.

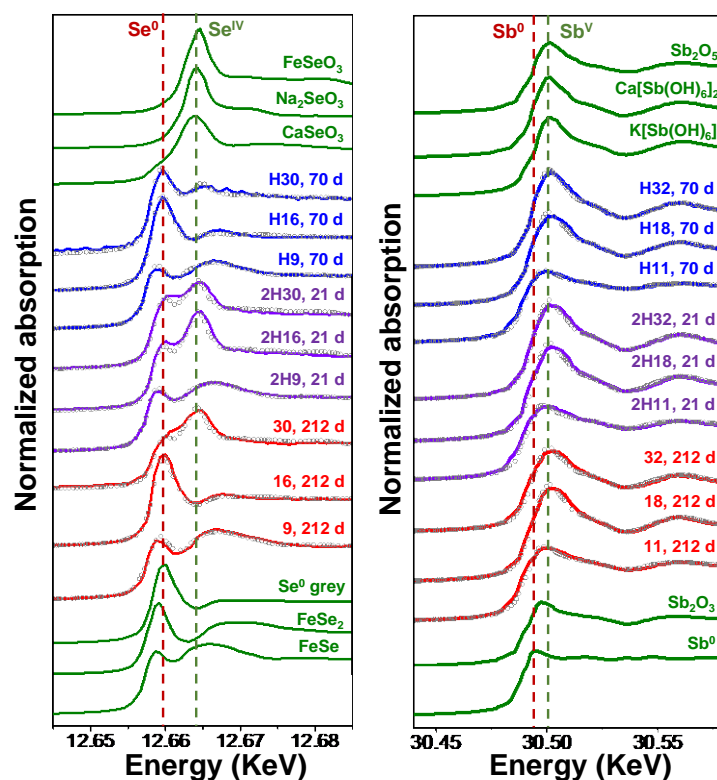


Figure 1. XANES spectra of sorption products on 3 Fe-couples, and reference compounds in N₂ and H₂ atmosphere. Left panel: Se K-edge XANES spectra. Right panel: Sb K-edge XANES spectra. The solid curves represent the experimental data and grey dots are the linear combination fit (LCF) results.

To conclude, results provide the relative concentration of each solid species, and facilitate the estimation of the “experimental” redox potential in the cement matrix, which could be confronted to theoretical Eh imposed by Fe solid couples. We hope to continue to study the redox competition behaviors among RNs on certain Fe-couples (fixed Eh values) and to confirm the presence of (Fe_xCa_{1-x})(OH)₂ phase at the steel/NZVI/water interface.

Reference

B. Ma *et al*, Evidence of multiple sorption modes in layered double hydroxides using Mo as structural probe. Submitted.