



	<b>Experiment title:</b> <b>Molybdenum speciation and coordination environment in green rust</b>	<b>Experiment number:</b> <b>30-02 1123</b>
<b>Beamline:</b> BM30B	<b>Date of experiment:</b> from: 13 April 2017 to: 18 April 2017	<b>Date of report:</b> Aug 2018
<b>Shifts:</b> 15	<b>Local contact(s): Olivier Proux</b> <b>Mauro Rovezzi</b>	<i>Received at ESRF:</i>
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#### **Background**

Reinforced cementitious structures in nuclear waste repositories act as barriers to attenuate the diffusion of radionuclides (RNs). On the interface between corroded steel and hydrated cement, green rust (GR) can probably be formed in suboxic environments, e.g., in nuclear waste repositories, under near-neutral to alkaline conditions. GR phases belong to the layered double hydroxides (LDHs) family, which prevalently has positively charged surface and exchangeable intercalated anions. LDHs, like AFm phases, have shown strong ability to immobilize RN anions by adsorption, or anion exchange, or co-precipitation [1-3]. Regarding GR, reduction on the surface or in the interlayer could be extra RN immobilization pathways. Besides, both radioactive and stable isotope species of Molybdenum (Mo) in the environment represent a potential threat to human's health. However, the behavior of Mo sorption on both cement hydration products and GR under anoxic conditions is still not well-documented. In this project, we aim to investigate  $\text{MoO}_4^{2-}$  sorption behavior on GR and cement hydration phases as a function of Mo concentration, to check different sorption sites on the edge of LDHs, which are functional prior to anion-exchange occurring.

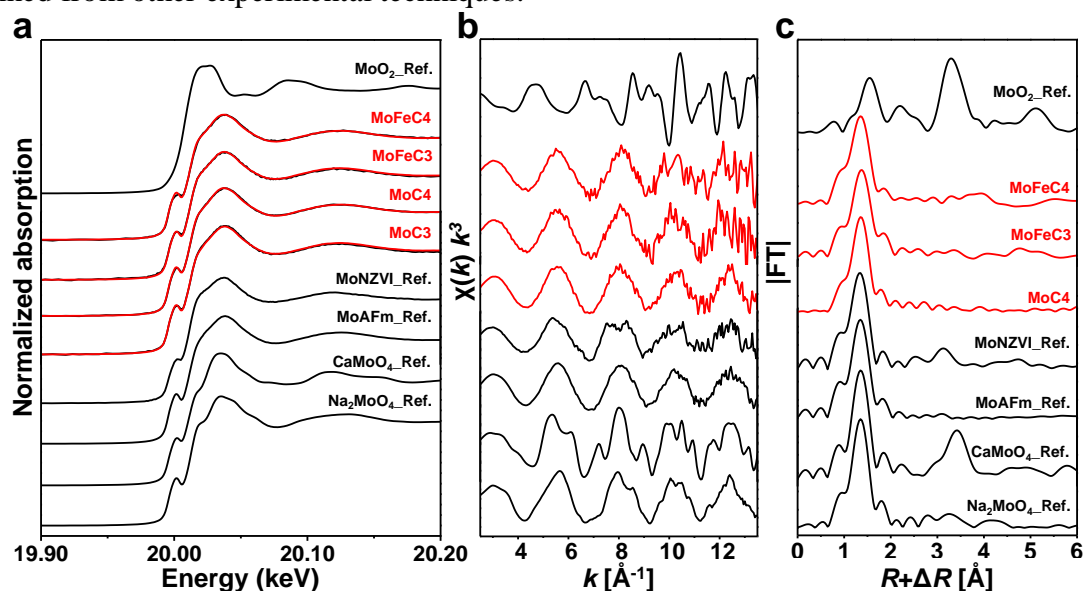
#### **Experiment**

In general, two series of molybdate ( $\text{MoO}_4^{2-}$ ) sorption products, 1) on diverse hydrated cement paste (HCP) and cement hydration products, and 2) on GR- $\text{Cl}_2$  and GR- $\text{SO}_4$ , were measured. Approximately, 50 samples (including references) were measured by EXAFS at Mo K-edge energy (20.0 keV). GR samples are very oxygen-sensitive, and their measurements were taken extreme care to avoid any oxidation. Prior to measurements, solids were collected, dried, and double side sealed by kapton tape under anaerobic condition. After, these samples were transported to the ESRF using an anaerobic jar. During measurements in the beamline, the samples were always stored in a  $\text{N}_2$ -filled glove bag, set up close to the hutch. Once needed to measure, samples were quickly fixed on the sample holder, which would be inserted into the orange cryostat soon. All samples were measured under ultra-high vacuum and liquid-He temperature. Data analysis was performed with Demeter system.

## Results

### 1) Mo(VI) sorption on different HCP and cement hydration products.

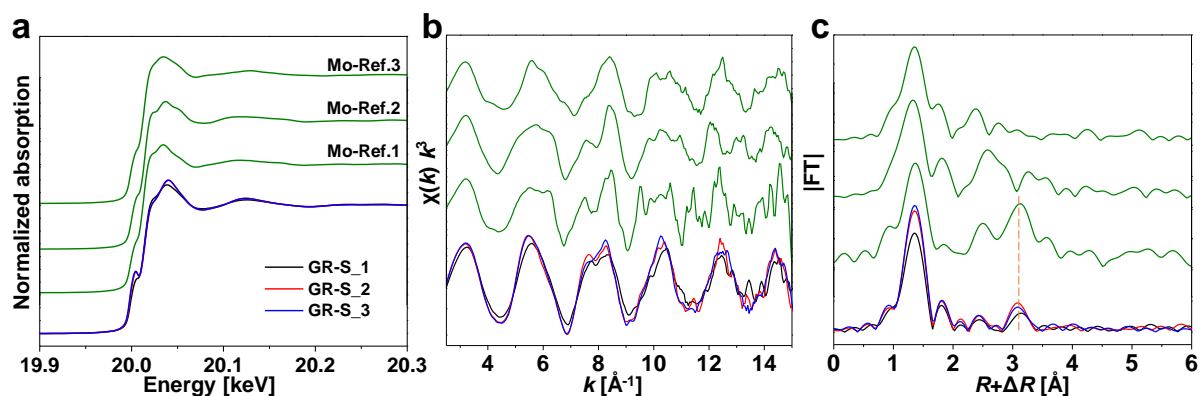
Different initial Mo(VI) loadings were studied. Sorption products from batch sorption experiments at higher initial loadings, and from reactors with two effective sorbents, together with Mo(VI) chemicals references, were measured by Mo K-edge XAS spectra (Figure 1). As shown, no Mo reduction can be detected. The LCF of normalized XANES spectra was performed and the fitting results indicated that sorption on NZVI and AFm phase predominated the solid Mo(VI) species in cement reactors. At high Mo loadings, more fractions of  $\text{Na}_2\text{MoO}_4$  were obtained based on the LCF. Furthermore, EXAFS were also collected and the  $k^3$ -weighted EXAFS oscillations were shown in Figure 1b. Due to diluted solid Mo concentrations, the oscillation noise was still quite strong at high  $k$  range, although 30-element Ge solid-state detector and very low measuring temperature ( $\sim 4$  K) was used. It can be concluded that mainly one oscillation frequency can be observed. Further neighbor shells may also exist in NZVI-bearing cement samples (Figure 1c). However, multiplicity of possible configurations or interfacial ill-coordinated Mo could weaken the EXAFS signal of further shells. Further EXAFS analysis will be performed, with the aid of information obtained from other experimental techniques.



**Figure 1.** Mo K-edge XAS spectra of Mo-sorbed cement samples and the references. (a) Normalized XANES spectra and the LCF results. (b)  $k^3$ -weighted EXAFS oscillations. (c) Fourier transformed (not corrected for phase shift) EXAFS signals.

### 2) Interaction between Mo(VI) and GRs at different reaction time.

High-quality XANES-EXAFS data were collected (Figure 2). The spectra of GR-SO<sub>4</sub> sorption products with different reaction time were labelled with GR-S-1, -2, and -3, for reaction at the initial, middle, and final stage, respectively. As can be seen, with reaction proceeding, the pre-edge peak intensity increased, indicating Mo coordination geometry changing from the distorted octahedral to the tetrahedral.  $k^3$ -weighted EXAFS oscillations were shown in Figure 2b, obvious oscillation frequency difference can be observed between GR-S-1 and the other two samples. This means that the coordination environment of Mo really changed with reaction time. After FT, the radial distributions were shown in Figure 2c. Regarding the second neighbor shell, the entire three samples showed quite strong backscattering signal at  $R+\Delta R \sim 3.1$   $\text{\AA}$ , which is quite close to the  $R$  peak position of Mo-Ref.1. It suggested that the coordination environment of Mo on GR-SO<sub>4</sub> is similar to that on Ref.1 material. Further structure refinement based on EXAFS oscillations is still proceeding, together with PDF analysis of HE-XRD for figuring out the dominant phases after reaction.



**Figure 2.** Mo K-edge XAS spectra of Mo sorption products on GR-SO<sub>4</sub>, and three reference materials. (a) Normalized XANES spectra. (b)  $k^3$ -weighted EXAFS oscillations. (c) Fourier transformed (not corrected for phase shift) EXAFS signals.

To conclude, almost all the XAS data were already successfully merged, calibrated, and normalized. The structure refinement of EXAFS results, combining with all the information from other experimental techniques, is still ongoing. Once completed, several papers will be concluded. These results will facilitate the comprehension of nuclide anions sorption behaviours on LDHs and the estimation of “experimental” active sites density. In nuclear waste disposal, anionic RNs can be adsorbed on different sites of LDHs and the adsorbed anions should possess distinct leaching behaviors. This work will give an insight to the sorption and desorption ability of RNs on LDHs under different concentrations.

## Reference

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