

Experiment Report Form



	Experiment title: Uranium carbonates interaction with layered double hydroxides	Experiment number: EV434
Beamline: BM20	Date of experiment: from: 13.11.21 to: 19.11.21	Date of report: 19.9.23
Shifts: 18	Local contact(s): Andreas C. Scheinost, Kristina O. Kvashnina, and André Rossberg	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Natalia Mayordomo, ^{1*} Thomas Zimmermann, ¹ Katharina Müller, ¹ André Rossberg, ^{1,2} Andreas C. Scheinost, ^{1,2} Elena Bazarkina, and Kristina Kvashnina. ^{1,2} ¹ Institute of Resource Ecology, Helmholtz-Zentrum Dresden – Rossendorf (HZDR), 01328, Dresden (Germany). ² ESRF, The European Synchrotron, 71 Avenue des Martyrs, CS40220, 38043 Grenoble Cedex 9, France.		

Report:

U is a natural occurring element used as fuel in nuclear energy production, mainly as the isotope ^{235}U with a half-life of $7.04 \cdot 10^8$ years.¹ Therefore, measures must be taken to prevent environmental U contamination, especially in U mining areas and in the context of nuclear waste management, e.g. in a deep geological repository. U(VI) immobilization by metal oxides and clay minerals increases with increasing pH (in absence of carbonate); as well, U(VI) immobilization is favoured when U(VI) is reduced to U(IV).^{1,2} However, under alkaline conditions and in the presence of carbonate, the U(VI) removal considerably decreases due to the formation of negatively charged U(VI)-carbonate species whose uptake by amphoteric minerals and clays is electrostatically hindered.³ The removal of such U(VI)-carbonate species is enhanced by the use of positively charged minerals, like layered double hydroxides (LDH).⁴ Thus, the focus of the measuring campaign was to analyze the molecular environment of uranium after being in contact with two different LDH: i) Fe(II)-Al LDH that can reduce U(VI) to U(IV), and ii) Ca-Al LDH that cannot promote the reduction of U(VI).

X-ray absorption spectroscopy (XAS) was used to measure the samples at BM20 at ESRF. Spectra were taken at the U M_4 -Edge (3,728 eV) high-energy resolved fluorescence detection – X-ray absorption near-edge structure (HERFD-XANES), and at the U L_{III} -Edge (17,166 eV) extended X-ray absorption fine structure (EXAFS) in fluorescence mode. The samples were cooled down to 15 K by using either a cryostream or a closed-cycle He cryostat, respectively. In total, 18 samples were measured at the U L_{III} -Edge and 4 samples at the U M_4 -Edge. For the sake of brevity this report is focused on the results obtained by Fe(II)-Al LDH. The main results are shown in Figure 1.

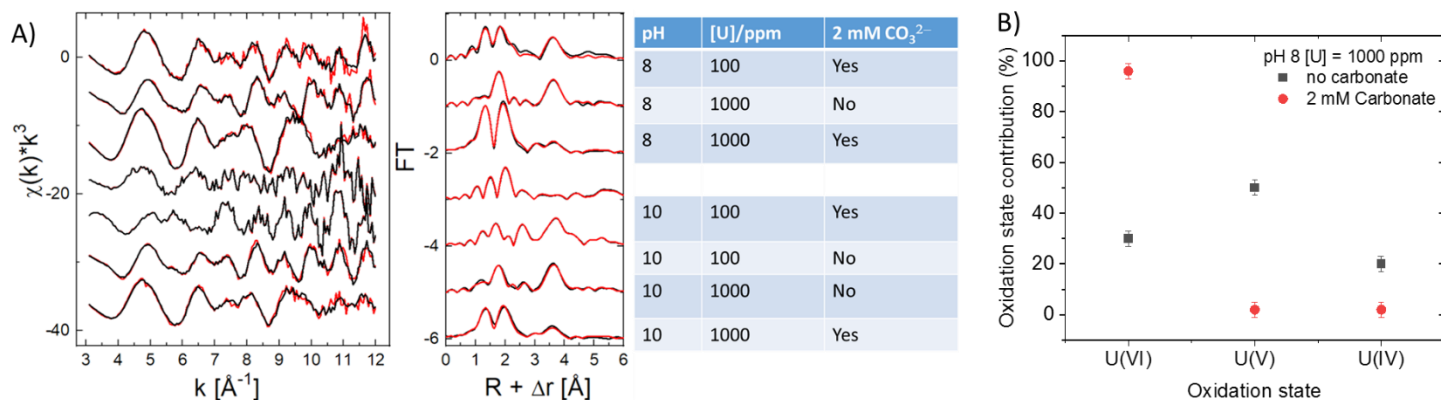


Figure 1. A) Fourier transforms (FT) of the U L_{III} -edge EXAFS spectra of U retained on Fe(II)-Al LDH for different U loadings, carbonate concentration, and pH values. B) Contribution of the different oxidation states of U obtained by iterative factor analysis for two spectra measured at the U M_4 -edge HERFD-XANES.

It is observed that the shape of the EXAFS spectra of U interaction with Fe(II)-Al LDH depends on the pH, and strongly depends on the presence of carbonate (Figure 1A). The experimental EXAFS data could be fit by linear combination of four components, among which, the most remarkable contribution corresponds to U(IV)O_2 and $\text{U(VI)O}_2(\text{CO}_3)_3^{4-}$. The U L_{III} -edge XANES spectra were evaluated to determine the contribution of the different oxidation states of U in the sample (not shown). The results show the presence of U(VI) and U(IV) in the samples, being the amount of U(IV) higher than U(VI) when carbonate is present. In addition to the EXAFS measurements, selected samples were measured by HERFD-XANES since it is a very suitable technique to differentiate the oxidation states of uranium. As example, the contribution of uranium oxidation states for two samples are shown in Figure 1B. It is shown that U(VI) exists when carbonate is present. On the contrary, when carbonate is excluded from the system, U-reduced species (as U(V) and U(IV)) are also present. The results obtained by EXAFS and HERFD-XANES indicate that the presence of U(VI)-carbonate species in solution inhibit the reduction of U(VI) to U(V) and/or U(IV). This observation is very relevant for the safety assessment of a nuclear waste repository and the development of U scavengers. Carbonate is an ubiquitous anion, and its presence has a clear effect on the mechanism responsible of U immobilization by redox active minerals, limiting the reduction of U(VI).

Up to date, the available works dealing with uranium immobilization by LDH do not have the focus on the immobilization of anionic U-carbonate species. The results obtained in the measuring campaign seed light on how the presence of carbonate highly influence the mechanisms of uranium removal by Fe(II)-Al LDH – and probably other redox-active minerals. This project is still in progress as it is needed to identify the other two minor components of the EXAFS spectra and to determine the origin of the differences observed by the two different techniques when quantifying the contribution of the oxidation states of U in the samples

References

1. Cumberland, S. A., Douglas, G., Grice, K. & Moreau, J. W. Uranium mobility in organic matter-rich sediments: A review of geological and geochemical processes. *Earth-Science Rev.* **159**, 160–185 (2016).
2. Gao, M., Zhu, G. & Gao, C. A Review: Adsorption Materials for the Removal and Recovery of Uranium from Aqueous Solutions. *Energy Environ. Focus* **3**, 219–226 (2014).
3. Marques Fernandes, M., Baeyens, B., Dähn, R., Scheinost, A. C. & Bradbury, M. H. U(VI) sorption on montmorillonite in the absence and presence of carbonate: A macroscopic and microscopic study. *Geochim. Cosmochim. Acta* **93**, 262–277 (2012).
4. Forano, C., Costantino, U., Prévot, V. & Gueho, C. T. Layered double hydroxides (LDH). in *Developments in Clay Science* **5**, 745–782 (Elsevier Ltd., 2013).