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## D3.3 – XAS Analyses of Coprecipitates and Evolution with Time of the Solid Phases

**SLOW PROCESSES IN CLOSE-TO-EQUILIBRIUM CONDITIONS FOR  
RADIONUCLIDES IN WATER/SOLID SYSTEMS OF RELEVANCE TO NUCLEAR  
WASTE MANAGEMENT  
SKIN**

### **COLLABORATIVE PROJECT (CP)**

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Dissemination Level

<b>PU</b>	Public	×
<b>RE</b>	Restricted to a group specified by the partners of the project	
<b>CO</b>	Confidential, only for partners of the project	



## 1. Introduction and Objectives

Task 3.1 is devoted to the study of the interaction between uranium and iron oxides.

Iron oxides are present in nature and also in the near and far field of the repository; they are the main products of canister corrosion and can be found among the engineered and geological barriers. Among the iron oxides, the amorphous ferrihydrite is one of the most widespread iron solids and an important precursor of more stable and crystalline iron oxides. Ferrihydrite is a poorly ordered iron oxide; its two extremes of crystal order are referred to as 2-line and 6-line ferrihydrite, because of the number of reflections shown in their respective XRD patterns (Cornell and Schwertmann, 2003).

The retention of radionuclides, U(VI) among them, by these Fe(III) solid phases has been long studied by different authors, mainly from the perspective of sorption equilibria. The long time frames of interest for the safety assessment, and the massive occurrence of iron compounds in the repository highlight the possibility of more intimate interactions between U(VI) and iron solid phases, that might be subjected to changes as the U(VI)/Fe(III) solids evolve with time.

Ferrihydrite evolution with time and the final products formed depend on many factors, such as pH, time, temperature, etc (George G., Pickering, I. (1995) EXAFSPAK: A suite of computer programs for analysis of X-ray absorption spectra. Stanford synchrotron Radiation Laboratory, Stanford, CA, USA.

Rehr J.J., Albers R.C. (2000) Theoretical approaches to X-ray absorption fine structure. *Reviews of Modern Physics*, 72, 621-654.

Ressler T. (1998) WinXAS: a program for X-ray absorption spectroscopy data analysis under MS-Windows. *Journal of Synchrotron Radiation*, 5, 118-122.

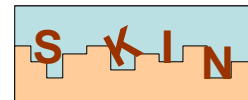
, Schwertmann and Murad, 1983, Schwertmann et al., 2004). The presence of foreign species such as U(VI) in the system will affect the ferrihydrite ageing process. Those foreign species can a) modify the rate of transformation, usually by slowing the process, and/or b) change the composition and properties of the end product (Cornell and Schwertmann, 2003).

The ageing and transformation process of ferrihydrite will in turn affect the solubility and the retention/release of uranium from the coprecipitates (Bruno et al., 1995, Duro, 1996). Finally, carbonate, that has a high affinity towards Fe, is expected to influence significantly the overall process (Bruno et al. 1992).

The objective of present work is to deepen in the understanding of bounding processes between uranium and iron oxides at long time frames, in order to evaluate the role of these solids in the retention and release of uranium from the repository.

## 2. Methodology

Fe(III)-U(VI) coprecipitates were prepared from  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solutions. Initial concentrations were  $[\text{Fe}] \approx 0.01 \text{ M}$  and  $[\text{U(VI)}] \approx 10^{-4} \text{ M}$  at  $\text{pH} = 5.5$ , that is, initial uranium concentrations were below theoretical schoepite solubility limit. Afterwards, the samples were aged in solution for periods between 1 day and 5 weeks. The solids were afterwards collected and let to age in dry state for periods between some days to 11 years before the analysis.



All the process (preparation, wet aging and dry aging) were carried out at room temperature. As a consequence, thermal transformations are not expected to occur.

The analysis of the solutions indicated that the uranium content in the coprecipitates was  $\approx 1-2\%$ .

Different spectroscopic techniques were used in order to characterize the precipitates:

-X-ray diffraction analyses (XRD) were performed in the X-ray laboratory of Institut de Ciències de la Terra Jaume Almera (CSIC) and in the X-ray diffraction service of the Universitat Autònoma de Barcelona (UAB).

-Iron Extended X-Ray Absorption Fine Structure analyses (EXAFS) were performed using the Fe K-edge signal in the A1 Beamline at the German Electron Synchrotron facility (DESY/Hasylab) in Hamburg. Spectra were collected in transmission mode at room temperature.

-Uranium EXAFS analyses were performed using the U  $L_{III}$ -edge in the Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble. Spectra were collected in fluorescence mode at room temperature.

-Micro X-ray fluorescence analyses ( $\mu$ -XRF) were performed in the L Beamline at the German Electron Synchrotron facility (DESY/Hasylab) in Hamburg.

EXAFS scans were collected, pre-treated and averaged using Sixpack (Webb, 2005). Data analysis was performed using the EXAFSPAK (George and Pickering, 1995) or the WinXAS (Ressler, 1998) software. Theoretical scattering amplitudes for each absorber and backscattered pair were calculated with the FEFF 8.20 code (Rehr and Albers, 2000).

$\mu$ -XRF data treatment was done using PyMca (Solé et al. 2007).

### 3. Main results

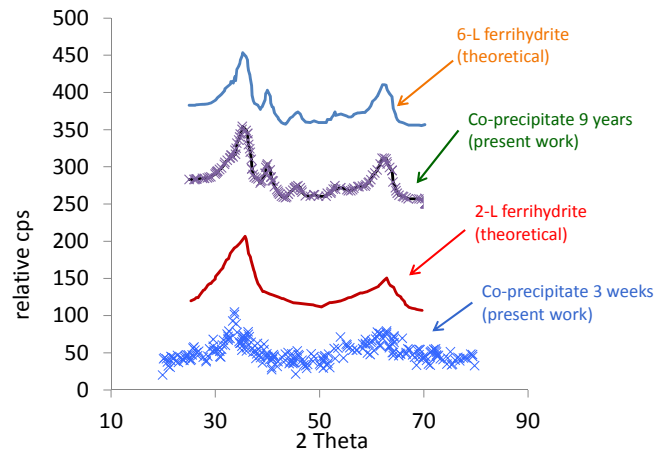
#### *The effect of uranium in the ferrihydrite ageing process*

The evolution of the U(VI)-Fe coprecipitates was studied with XRD and with iron EXAFS analyses using the Fe K-edge signal.

As shown in Figure 1, the XRD spectrum for a sample aged 3 weeks was similar to that of a 2-line ferrihydrite. On the contrary, the spectrum of a 9 years aged sample resembled that of a 6-line ferrihydrite.

Similar conclusions were obtained with the iron EXAFS analyses. The spectra of the samples aged for 1 and 3 week resemble that of a 2-line ferrihydrite; nevertheless, the spectrum of the 7 year sample has some distinct features that indicate the evolution towards a 6-line ferrihydrite.





**Figure 1.** Crosses: Results of the XRD measurements for samples aged 3 week and 9 years (present work). Solid lines: XRD spectra for 2-line (red) and 6-line (blue) ferrihydrite, from Zhao et al. (1994).

*The effect of ageing in the retention of uranium in the coprecipitates*

The ageing process of the coprecipitates and the evolution of the bulk solid structure are expected to have an influence on the retention of uranium within them. EXAFS analyses using the U L<sub>III</sub>-edge signal for samples aged from 1 day to more than 10 years were performed to investigate this process.

Some slight differences are observed in the spectra as the ageing time of the coprecipitates increases (see some examples in Figure 2), suggesting that the uranium environment might change with time.

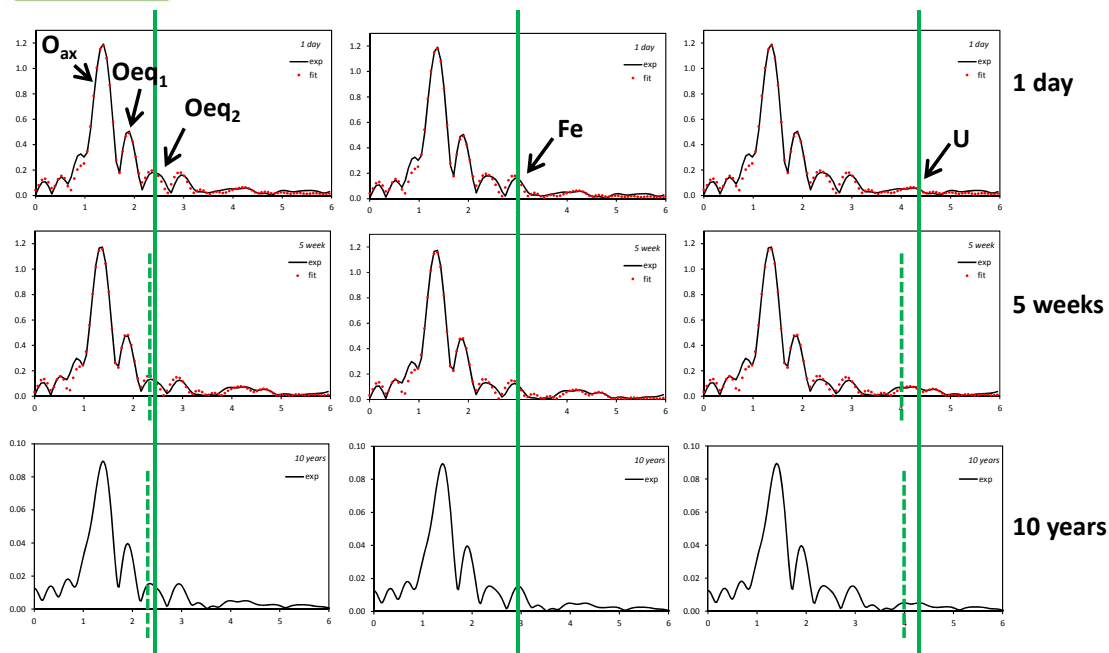
The uranium EXAFS spectrum of the coprecipitates shows several coordination shells (Figure 2). The relevant changes observed are described below.

- The third coordination shell also seems to correspond to the uranium interaction with an oxygen in the equatorial plane (O<sub>eq2</sub>). The distance between uranium and this atom seems to progressively decrease with the ageing time.

- Preliminary fittings indicate that the U-Fe coordination number decreases with time.

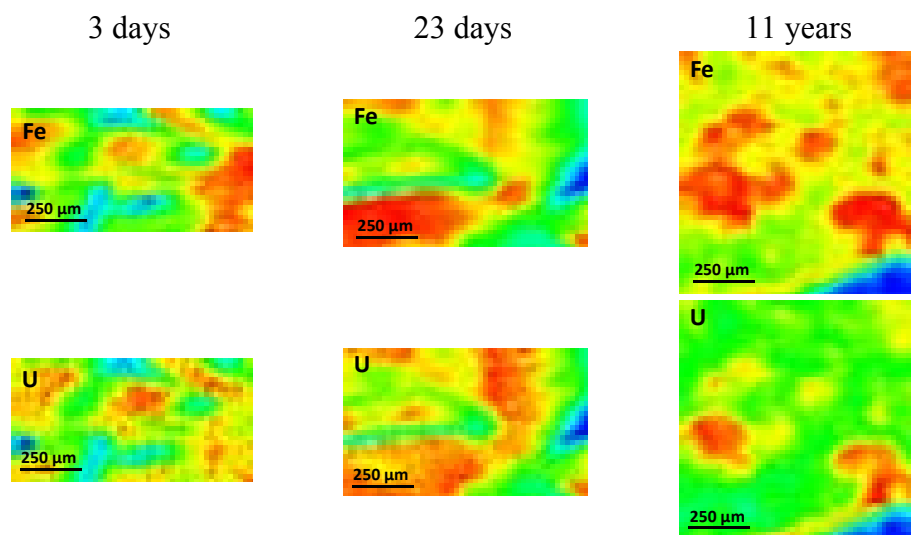
- U-U interaction (fifth coordination shell) is difficult to appreciate in some of the spectra, due to noisy background and the long interaction distances between those atoms. However, the U-U distance seems to decrease with the aging time, getting close those U-U distances in schoepite. Furthermore, preliminary fits also point out that the U-U coordination number could increase with time.

Those measurements are consistent with a re-arranging of the uranium content towards a schoepite-like structure.



**Figure 2.** Results of the EXAFS U  $L_{III}$ -edge measurements for U(VI)/Fe(III) coprecipitates at different ageing times. Solid black lines are experimental data; red dots indicate fittings (when available). Green lines indicate peak displacement (see text).

In order to observe the distribution of the elements (Fe, U) in the different ageing samples  $\mu$ -XRF analyses were performed. The results are shown in Figure 3. As shown in the  $\mu$ -XRF results, the samples are highly heterogeneous. Nevertheless, uranium measurements are consistent with a regrouping of the uranium content as ageing time increases, being the difference most significant in the 11 years aged sample (Figure 3) when compared with samples aged for 3 or 23 days.



**Figure 3.** Results of the  $\mu$ -XRF measurements for U(VI)/Fe(III) coprecipitates at different ageing times. Up) Iron. Down) Uranium. Colours provide a qualitative indication of the concentration of the different elements in the samples (red: high concentration; blue: low concentration).

## 4. Conclusions and further work

The results presented indicate that the presence of uranium is changing ferrihydrite reactivity towards internal ordering, pointing out an evolution from a 2-line ferrihydrite towards a 6-line ferrihydrite. This type of transformation is probably related to the presence of the foreign cation (U(VI)) in the system

Uranium is also affected by the ageing process, and the results indicate a re-arranging of the uranium content towards a schoepite-like structure. This would imply that the assessment of the efficiency of this retention process at long time frames would be given by the schoepite solubility limit.

## 5. Acknowledgement

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