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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Coprecipitation behaviour of uranium onto ferrihydrite	**Experiment number**: 20-01 716
Beamline: BM20	**Date of experiment**: from: 31/October/2012 to: 03/November/2012	**Date of report**: January 2013
Shifts: 9	**Local contact(s)**: Andre Rossberg	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Mireia Grivé

Elisenda Colàs*

Alba Valls*

Amphos 21. Pg. Garcia i Faria 49-51, 08019 Barcelona (Spain)

Introduction

Sorption, coprecipitation or formation of solid solutions are likely to be the dominant mechanisms of metal uptake by iron oxides. The retention of radionuclides, U(VI) among them, by these Fe(III) solids are of high interest for the safety assessment of radioactive waste disposal, due to the massive occurrence of iron compounds in the repository as one of the main steel corrosion products or due to its widespread presence among the surrounding materials.

In order to evaluate the importance of these processes in the sequestration or mobilization of radionuclides, it is necessary to understand how uranium is bound to the iron solids and how ageing time does influence the retention and the rearrangement processes of the precipitates. The objective of this work is therefore to investigate the main evolving processes with ageing time of synthetic coprecipitated samples of Fe(III) oxyhydroxides and U(VI), using XAS analysis.

Experimental

Fe(III)-U(VI) coprecipitates were prepared from Fe(III) nitrate and U(VI) nitrate solutions. Initial concentrations were [Fe]≈0.01 M and [U(VI)]≈10^{-4} M at pH≈5.5, that is, initial uranium concentrations were below theoretical schoepite solubility limit. 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. The analysis of the solutions indicated that the uranium content in the coprecipitates was ≈1-2%.

Uranium EXAFS analyses were performed using the U L_{III}-edge in the Rossendorf Beamline (ROBL, BM20) at ESRF. Spectra were collected in fluorescence mode at room temperature. EXAFS scans were collected, pre-treated and averaged using Sixpack (Webb, 2005). Data analyses were performed using 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).

Results

EXAFS analyses using the U L_{III}-edge signal for samples aged from 1 day to 11 years are shown in Figure 1. Some differences are observed in the spectra as the ageing time of the coprecipitates increases, suggesting that the uranium environment might change with time.

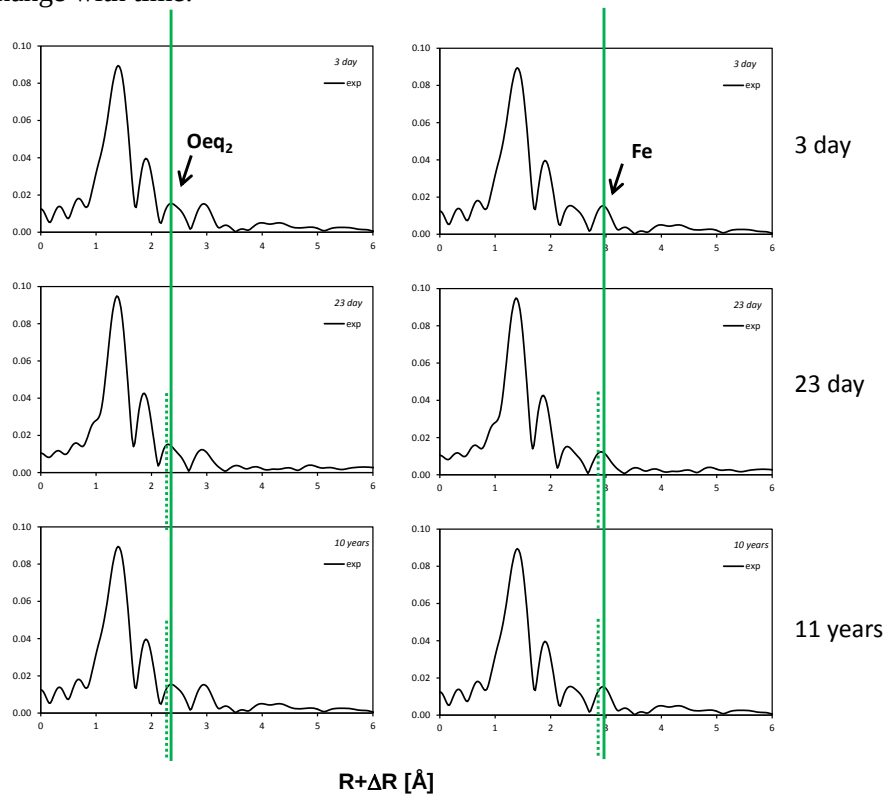

Figure 1. Results of the EXAFS U L_{III}-edge measurements for U(VI)/Fe(III) coprecipitates at different ageing times. Solid black lines are experimental data. Green solid lines indicate peak position at short ageing tines; green dotted lines indicate peak displacement as the ageing evolves.

The uranium EXAFS spectrum of the coprecipitates shows several coordination shells (Figure 1):
-The most intense feature in the spectrum corresponds to the two axial oxygen atoms of the uranyl group.
-The second coordination shell corresponds to the uranium interaction with oxygen atoms in the equatorial plane.
-The third coordination shell also seems to correspond to the uranium interaction with an oxygen in the equatorial plane (Oeq2). The distance between uranium and this atom seems to progressively decrease with the ageing time of the co-precipitate sample.
-Preliminary fittings also indicate that the U-Fe coordination number decreases with time.
-U-U interaction is difficult to appreciate due to noisy background and the long interaction distances between those atoms.

Those measurements are consistent with a re-arranging of the uranium content towards a schoepite-like structure. This hypothesis is in agreement with preliminary data obtained with other spectroscopic techniques (X-ray diffraction, μ-XRD and iron EXAFS analyses), which also point out to an evolution of the coprecipitates with the ageing process. Further data analyses and fitting of the U-L_{III} EXFAS spectra are still on-going.

References

- Rehr, J. J. and Albers, R. C. Rev. Mod. Phys. 2000, 72, 621–654.
- Ressler, T. J. Synchrotron Radiat. 1998, 5, 118–122.
- Webb, S.M. Physica Scripta, 2005, T115, 1011-1014.

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