



D3.2 – Report on Sample Preparation and Study of the Kinetics of U Dissolution from U/Fe Coprecipitates

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

PU	Public	X
RE	Restricted to a group specified by the partners of the project	
CO	Confidential, only for partners of the project	

1. Background

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

The interaction between uranium and iron solid phases is very relevant especially for the near but also for the far-field of a deep nuclear waste repository. The materials of the containment are steel-based and therefore, the corrosion products of iron may actively retain radionuclides by sorption and by coprecipitation processes. Iron(III) solid oxides are not only important in the safety case by their presence as corrosion products in the steel-based containers, but also because of their ubiquity in the geosphere and the active dynamics of their oxidation-reduction processes.

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.

The objectives of task 3.1 are deepening in the understanding of the interactions between U(VI) and Fe(III)-oxyhydroxides and the evolution of these interactions with time. The effect of carbonate on this system and its implications are also studied.

2. Introduction and Objectives

Among the iron oxides resulting from the corrosion processes of the canister and present in some of the engineered and geological barriers, the amorphous *ferrihydrate* is one of the most widespread iron solids and an important precursor of more stable and crystalline iron oxides such as goethite or hematite. The ferrihydrate evolution with time and the final products formed depends on many factors, such as pH, time, temperature, etc (Schwertmann et al., 1999, Schwertmann and Murad, 1983, Schwertmann et al., 2004). The presence of foreign species (such as uranium) in the system will affect the ferrihydrate ageing process. The ageing and transformation process of ferrihydrate will affect in turn the solubility and the retention/release process of uranium from the coprecipitates (Bruno et al., 1995, Dodge and Francis, 2002, Duro, 1996, Smith et al., 2009).

The objective of this work is to deepen in the understanding of bonding 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.

3. Methodology

Several U(VI)-Fe(III) coprecipitates were prepared by alkaline co-precipitation of U(VI) ($\approx 1-2\%$) with Fe(III) homogeneous solutions ($I=0.1$ M). Samples were aged at room temperature (under N_2 atmosphere) in aqueous solutions at different time intervals, from days to 5 weeks. After 5 weeks of wet aging, two additional samples were stored under dry conditions and aged for several years.

The precipitates were analysed using X-ray diffraction (XRD) and Extended X-Ray Absorption Fine Structure (EXAFS).

XRD analysis was 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 EXAFS analyses were performed using the Fe K-edge signal in the A1 Beamline at the German Electron Synchrotron facility (DESY/HASYLAB) in Hamburg. Uranium EXAFS analysis were performed using the U L_{III}-edge in the Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble.

4. Main results

The main *results* are summarized below.

1. According to the XRD analysis of the samples aged at 3 weeks and 9 years, the bulk of U(VI)-Fe(III) coprecipitates can be assumed to evolve from a 2L ferrihydrite (3 weeks aged sample) to a 6L ferrihydrite-like (9 years aged sample) structure. Similar results were obtained by Kukkadapu and co-workers (Kukkadapu et al., 2003) for Ni(II)-Fe(III) coprecipitates.
2. The results obtained in the EXAFS (Fe K-edge) measurements were consistent with the XRD results.
3. The results obtained in the EXAFS (U L_{III}-edge) measurements indicate 3.41-3.46 Å U-Fe distances. These distances are consistent with an edge-sharing bond between U(VI) and ferrihydrite.
4. The results obtained in the EXAFS (U L_{III}-edge) measurements indicate that the bonding environment of uranium in the coprecipitates evolves with ageing time, towards a schoepite-like structure.

A U-O_{eq}2 at a distance of 2.85-2.90 Å has been identified. The distance decreases with time and appears near the U-O_{eq} distance of that corresponding to schoepite.

The evolution of 4.0-4.3 Å U-U distance measured in previous works (Grivé, 2005) indicates that the distance decreases with time, approaching schoepite-like distances.

The *preliminary conclusions* are the following:

1. The retention of U(VI) within the structure of a Fe(III) oxyhydroxide like solid remains effective even after 5 weeks of suspension and after 9 years of a dry-stored sample.
2. The re-arranging of the uranium content towards a schoepite-like structure might suggest that the assessment of the efficiency of the uranium retention process at relative long time frames would be given by the schoepite solubility limit. As a consequence, uranium solubility at these time frames could be expected to be controlled by the solubility of schoepite.

Further work will be focused on:

- μ -XAS analysis (Hasylab, beamline L HYMO, proposal accepted) in order to better understanding the distribution of the elements in the sample and make a mapping of the U distribution and rearrangement in the different aged coprecipitates.
- Study the effect of carbonate on the coprecipitate ageing process.

References

- Bruno, J., DePablo, J., Duro, L., and Figuerola, E. (1995). Experimental study and modeling of the U(VI)-Fe(OH)₃ surface precipitation/coprecipitation equilibria. *Geochimica et Cosmochimica Acta*, 59(20):4113–4123.
- Cornell, R. M. and Schwertmann, U. (2003). *The iron oxides. Structure, properties, reactions, occurrence and uses*. VCH, second edition edition.
- Dodge, C. and Francis, A. (2002). Photodegradation of a ternary iron(III)-uranium(VI)-citric acid complex. *Environmental Science & Technology*, 36(9):2094–2100.
- Duro, L. (1996). *Estudio cinético y termodinámico de la interacción entre U(VI) y oxihidróxidos de Fe(III)*. PhD thesis, UB.
- Grivé, M. (2005). *The linkage between uranium, iron and carbon cycling processes at interfaces: evidences from combined solution chemical and spectroscopic studies*. PhD thesis, Universitat Politècnica de Catalunya.
- Kukkadapu, R., Zachara, J., Fredrickson, J., Smith, S., Dohnalkova, A., and Russell, C. (2003). Transformation of 2-line ferrihydrite to 6-line ferrihydrite under oxic and anoxic conditions. *American Mineralogist*, 88(11-12):1903–1914.
- Schwertmann, U., Friedl, J., and Stanjek, H. (1999). From Fe(III) ions to ferrihydrite and then to hematite. *Journal of colloid and interface science*, 209:215–223.
- Schwertmann, U. and Murad, E. (1983). Effect of pH on the formation of goethite and hematite from ferrihydrite. *Clay Minerals*, 31(4):277–284.
- Schwertmann, U., Stanjek, H., and Becher, H. (2004). Long-term in vitro transformation of 2-line ferrihydrite to goethite/hematite at 4, 10, 15 and 25°C. *Clay Minerals*, 39(8):433–438.
- Smith, S. C., Douglas, M., Moore, D. A., Kukkadapu, R. K., and Arey, B. W. (2009). Uranium extraction from laboratory-synthesized, uranium-doped hydrous ferric oxides. *Environmental Science & Technology*, 43(7):2341–2347.