

Uranium incorporation during iron (oxyhydr)oxide crystallisation at hyperalkaline pH

T. A. MARSHALL^{1*}, G.T.W. LAW², K. MORRIS²,
J.F.W. MOSSELMANS³ AND S. SHAW¹.

¹ESSI, School of Earth and Environment, University of Leeds, UK.
teetam@leeds.ac.uk (*presenting author)

²RCRD and CRR, Schools of Earth, Atmospheric and Environmental
Sciences and Chemistry, The University of Manchester, UK.

³Diamond Light Source, UK.

Geological disposal of the legacy of radioactive wastes stored at Earth's surface is now the accepted management pathway for these materials and is a task of importance for nuclear power generating countries. In many radioactive waste disposal scenarios, intermediate level wastes are grouted and the geological disposal facility (GDF) will have cement present as a ubiquitous engineering material. Further, cementitious grouts have been considered as backfill for the GDF. Therefore, post-closure leaching of cementitious materials in a GDF is expected to create hyperalkaline conditions in and around the repository. These high pH fluids will react with the repository components and host rock, resulting in mineral alteration and crystallisation. Iron within the host rock derived from the alkaline breakdown of Fe-bearing silicate minerals (e.g. biotite, chlorite) or corrosion products formed within the repository will form iron (oxyhydr)oxide minerals. The formation and re-crystallisation of these reactive minerals, which may sequester radionuclides through reduction to less soluble forms and/or incorporation to more stable secondary iron oxide phases [1], may prove key to the fate of radionuclides in such environments.

To evaluate the significance of these processes, ferrihydrite was crystallised under CO₂-free oxic and anoxic conditions, in two U(VI) amended synthetic cement leachates, representing early (pH 13.1) and late (pH 10.5) stage cement evolution for a cementitious ILW GDF. Under oxic conditions ferrihydrite crystallised to hematite (pH 10.5) and goethite (pH 13.1). Under anoxic conditions in both leachates, and in the presence of Fe(II), ferrihydrite crystallised to magnetite. X-ray Absorption Spectroscopy was used to characterise uranium association with each of the iron (oxyhydr)oxide phases during the crystallisation reactions. Under oxic conditions at pH 10.5, U(VI) rapidly (hours) sorbed to the ferrihydrite. Thereafter, during crystallisation, analysis indicates that U(VI) became structurally incorporated in the hematite lattice. At pH 13.1, U(VI) remained 0.22 µm soluble and did not sorb to either ferrihydrite or goethite. Under anoxic conditions, in both leachates, uranium was rapidly (minutes) removed from solution as the ferrihydrite crystallised to magnetite (catalysed by Fe(II) in solution). Here, U(VI) was reduced to U(IV) and XAS analysis suggests it was directly substituted into octahedral sites of the magnetite structure.

These data have significant implications for the safety case for uranium behaviour in alkaline conditions in a GDF and in contaminated land scenarios. Details of uptake and bonding mechanisms of uranium in the iron oxide phases will be presented.

[1] Boland et al. (2011) *Environ. Sci. Technol.* **45**, 1327-1333.

Advanced Geological Applications Using XRF Elemental Mapping and Small Spot Analysis

Al Martin^{1*}, Didier Bonvin², Chris Shaffer³, Kurt Juchli⁴

¹Thermo Scientific, The Woodlands, TX, USA,
al.martin@thermofisher.com (* presenting author)

²Thermo Fisher Scientific, Ecublens, Switzerland,
Didier.bonvin@thermofisher.com

³Thermo Fisher Scientific, Ecublens, Switzerland,
Christopher.shaffer@thermofisher.com

⁴Thermo Fisher Scientific, Ecublens, Switzerland,
kurt.juchli@thermofisher.com

23d. General geochemistry

Geochemical and R&D applications offer interesting analytical challenges in the sense that these materials can represent a wide elemental coverage, wide concentration ranges and varied sample matrices and sizes. Analytical performance of wavelength dispersive X-ray fluorescence (WDXRF) instruments is being constantly advanced in order to cope with such challenges.

While traditionally WDXRF technique has always demanded homogeneous samples, the latest developments permit analysis of small spots down to 0.5mm as well as mapping of a selected area of a sample. These new possibilities open up the WDXRF technique to heterogeneous samples where segregations, defects or inclusions can now be determined. Coupling these capabilities with standardless analysis permits quantification of up to 79 elements of the periodic table on selected points of the sample.

In this presentation, several examples will be presented and finally tied into one thorough application in which the power and flexibility of new WDXRF instruments are fully exploited.