

The incorporation of uranium into Fe(II)/Fe(III) (oxyhydr)oxide phases

H. E. Roberts,¹ K. Morris,¹ G. T. W. Law,² P. Bots,¹ J. F. W. Mosselmans,³ and S. Shaw¹

¹*School of Earth, Atmospheric and Environmental Sciences, Univ. of Manchester, M13 9PL, UK.*

²*School of Chemistry, Univ. of Manchester, M13 9PL, UK.*

³*Diamond Light Source Ltd, Didcot, OX11 0DE, UK.*

The current policy for the disposal of higher activity radioactive wastes in the UK is within a deep geological disposal facility (GDF). Here, within the engineered environment and over long timescales, the anaerobic corrosion of steel from storage canisters and engineering structures within a GDF will lead to the formation of a number of solid phases, including magnetite ($\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$) and green rust ($\text{Fe}^{\text{II}}_3\text{Fe}^{\text{III}}(\text{OH})_8\text{Cl}/n\text{H}_2\text{O}$). U(VI) adsorption and reduction to U(IV) can occur on the mineral surfaces limiting its environmental mobility.^{1,2} However, it is also clear that adsorbed U(IV) surface species can be easily remobilised through oxidation. Recently, incorporation of U into iron (oxyhydr)oxide structures has been proposed as a pathway to irreversibly bind U in the mineral structure.^{3,4} Despite the strong potential benefit of limiting U mobility in the environment through incorporation, the mechanism(s) of uranium incorporation into key Fe(II)/Fe(III) (oxyhydr)oxide phases such as magnetite and green rust are poorly understood.

In this study, magnetite and green rust were synthesized at a range of starting Fe(II):Fe(III) ratios (0.5-2.0) via a direct co-precipitation method in the presence of U(VI). X-ray diffraction analysis showed the reaction products consist of magnetite (Fe(II):Fe(III) = 0.5 and 0.6) and green rust (Fe(II):Fe(III) = 0.8 and 2.0). EXAFS spectroscopy confirmed that U was present as a mixture of U(IV)O₂ and uranium directly substituted for octahedrally coordinated U in the magnetite structure with XANES spectroscopy suggesting that incorporated U may be present as U(V). For green rust, U(VI) was also reduced to both U(IV)O₂ and as U incorporated within the Fe(II)/Fe(III) octahedral sites of the layer double hydroxide structure. Again, XANES analysis suggested this incorporated U was present as U(V) in the green rust structure. Acid dissolution experiments provided additional evidence that significant incorporation of U into the iron (oxyhydr)oxide phases was occurring.

Overall, these results confirm that U can be directly incorporated in the structures of both magnetite and green rust, which may offer a significant new pathway for U immobilisation in contaminated land and geological disposal systems.

References

1. Latta, D. E., Gorski, C. A., Boyanov, M. I. *et al.* Influence of Magnetite Stoichiometry on U VI Reduction. *Environ. Sci. Technol.* 46, 778–786 (2012).
2. Latta, D. E., Mishra, B., Cook, R. E. *et al.* Stable U(IV) complexes form at high-affinity mineral surface sites. *Environ. Sci. Technol.* (2014).
3. Marshall, T. A., Morris, K., Law, G. T. W. *et al.* Incorporation of uranium into hematite during crystallization from ferrihydrite. *Environ. Sci. Technol.* (2014).
4. Kerisit, S., Felmy, A. R., Ilton, E. S. Atomistic simulations of uranium incorporation into iron (hydr)oxides. *Environ. Sci. Technol.* 45 (7), 2770–2776 (2011).

Email corresponding author: sam.shaw@manchester.ac.uk