

Controls on the fate and speciation of Np(V) during iron (oxyhydr)oxide crystallisation

P. BOTS^{1*}, S. SHAW¹, G. T. W. LAW², T. A. MARSHALL¹,
J. F. W. MOSSELMANS³ AND K. MORRIS¹

¹SEAES, The University of Manchester, Manchester, M13 9PL, UK (*correspondence: pieter.bots@manchester.ac.uk).

²School of Chemistry, The University of Manchester, Manchester, M13 9PL, UK.

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

Neptunium-237 (Np) is a transuranic isotope produced in the nuclear fuel cycle (half-life = 2.13×10^6 y) and will be present in radioactive wastes. Under oxic conditions, it dominantly exists as neptunyl (Np(V)O_2^+), potentially the most mobile actinide species at nuclear legacy sites and in geodisposal systems. To date, studies have reported NpO_2^+ interactions with mineral surfaces [e.g. 1], however recent work has shown that actinyl species (e.g. UO_2^{2+}) can incorporate into iron oxides [2]. This study aims to characterize NpO_2^+ interaction with, and incorporation into iron oxides during crystallisation. In particular, for this study we focus on the alkaline geochemical conditions persistent at nuclear legacy sites, and relevant to intermediate level radioactive waste geodisposal.

We performed experiments to determine the interaction of NpO_2^+ with the crystallisation of ferrihydrite to hematite and goethite at pH = 9.5 – 13 [2]. We applied chemical extraction, solid phase characterization (TEM, XRD) and synchrotron based X-ray absorption spectroscopy (XAS) to identify and characterize the fate and local coordination environment of NpO_2^+ during the crystallisation. When NpO_2^+ was added to systems prior to ferrihydrite crystallisation and pH \leq 11, both the chemical extraction and XAS data showed the Np was incorporated in the mineral particles. Specifically, the EXAFS indicated that NpO_2^+ was directly substituted for Fe in the hematite (and goethite). Conversely, at pH = 13, chemical extractions suggested NpO_2^+ was weakly bound to goethite, and EXAFS suggested it was surface associated presumably as an adsorbed species or surface precipitate. These results indicate that the changes in speciation of Np(V) during ferrihydrite crystallisation will limit the mobility of NpO_2^+ in natural and engineered environments.

[1] Müller et al., *Environ. Sci. Technol.* (2015). [2] Marshall et al., *Environ. Sci. Technol.* **48**, 11853–11862 (2014).