

BIGRAD: Uranium(VI) Nanoparticles in Geodisposal Relevant Conditions

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In many countries a significant legacy of radioactive wastes exists. The strategy for radioactive waste management includes, for intermediate level wastes, containment in a Geological Disposal Facility (GDF) in the deep sub-surface which typically will contain cementitious materials. Interaction of groundwater with the cement and wastes will form a plume of a hyperalkaline leachate (pH 13 – 10) [1]. Under these conditions, thermodynamic modelling predicts that U(VI) solubility will be limited (ppb or lower) and controlled by equilibrium with alkali and alkaline-earth uranates [2]. In addition to transport in the dissolved phase, colloidal transport of radionuclides may be significant [3]. However, the potential formation of hexavalent uranium (U(VI)) colloids has received little interest despite the observation that U(VI) will be stabilised at elevated pH conditions relative to U(IV) [4]. Here, we focussed on the formation and characterisation of such colloidal phases.

We applied conventional geochemical and microscopy techniques combined with synchrotron based *in-* and *ex-situ* X-ray techniques (SAXS and XAS) to identify and characterize colloidal U(VI) nanoparticles in a synthetic cement leachate (pH \approx 13) with 10-60 ppm U(VI). The results show that in the 10 ppm system, 1-60 nm U(VI) nanoparticles formed within hours and remained stable as colloids for at least 2.5 years and in the presence of several mineral phases. Additional structural analyses showed that the nanoparticles had a clarkeite (Nauranate) type structure. Understanding the formation of such colloidal U(VI) nanoparticles is essential in understanding and constraining the behaviour of U in cementitious GDFs.

[1] Small and Thompson (2009) *Scientific Basis for Nuclear Waste Management* **1124**, 327-332 [2] Gorman-Lewis *et al* (2008) *J. Chem. Thermodyn.* **40**, 980-990 [3] Silva and Nitsche (1995) *Radiochim. Acta.* **70-1**, 377-396 [4] Gaona *et al* (2012) *Appl. Geochem.* **27**, 81-95