Plutonium Leaching from Cemented Radioactive Waste

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One of the most challenging components of the UK nuclear legacy is Magnox sludge arising from corrosion of Mg alloy-clad irradiated U metal fuel in high pH storage ponds. The sludges mainly comprise Mg hydroxide and carbonate phases, contaminated with fission products and actinides, including Pu. Cementation and deep geological disposal is one option for the long-term management of this material but there is a need to understand how Pu may be leached from this material if it is exposed to groundwater. Here, we show that leached samples of cemented $Mg(OH)_2$ powder prepared with Pu(IV)aq produce a visibly altered 'leached zone', penetrating several hundred microns into the sample, and showed slow leaching of Pu ($< 1.1 \times 10^{-6}$ day^{-1}).

Synchrotron Micro X-ray fluorescence mapping identified decreased Pu concentration within the 'leached zone'. Comparison of micro X-ray absorption spectroscopy (μ-XAS) spectra collected at positions with different cement chemistries in both leached and unleached samples showed no significant variation and indicated Pu was present in the same oxidation state and coordination environment. Linear combination fitting of XANES spectra to standards and EXAFS modelling showed the Pu was present as a mixture of 47% Pu(IV) and 53% Pu(V). The change of Pu oxidation from that in the stock solution, suggests partial Pu oxidation occurred during sample preparation. The similarity of XAS spectra from all sample positions, with different local chemistries, indicated the Pu oxidation state was not perturbed by the macro-scale variations in cement chemistry, surface oxidation, sample aging, or the leaching treatment. These experiments have demonstrated the potential for leaching of Pu from cementitious waste forms and the underlying significance requires further investigation.