Nuclear Energy Futures CDT

PhD Studentship Inducing the resumption of alteration in UK radioactive waste glasses.

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Background
The dissolution rate of radioactive waste glasses reduces by approximately a factor of one thousand over the first 1 – 28 days of contact with water. This reduction in dissolution rate, to what is known as the *residual rate*, is associated with a reduction in the thermodynamic driving force for dissolution (as solubility limits of certain glass components are approached and no more glass can be dissolved) and the protective effect on the glass surface of the formation of an altered layer that inhibits transport to and from the unaltered glass surface. A phenomenon that is occasionally observed at long time scales in international (and compositionally different) glass formulations is that glass dissolution resumes at rates approaching the initial dissolution rate. This phenomenon is known as *resumption of alteration* and remains as a potential uncertainty in the long-term performance of radioactive waste glasses in a geological disposal facility. This research project will investigate the applicability of a *resumption of alteration* scenario for UK radioactive waste glasses and determine the primary controls on any resumption with respect to their compositional differences from international radioactive waste glasses.

Objectives
The resumption is thought to occur when the thermodynamic driving force for the dissolution resumes as solution components form secondary phases on the surface of the glass. This secondary phase formation may also cause changes to the protective nature of the surface. The two main objectives of the project will be:

- Distinguish between the relative importance of the two effects thought to cause resumption of alteration.
- Determine the mechanism of the resumption of dissolution and its rate with respect to the initial rate and the rate-drop.
- Determine the sensitivity of the process to pH. This is to cover potential scenarios where groundwaters have become highly alkaline through contact with cementitious material in back-fill or ILW vaults.

Methods
In addition to conventional measurements of solution concentrations, detailed analysis of the surface material will be undertaken using scanning electron microscopy, EDX and microprobe analysis. Solid-state nuclear magnetic resonance spectroscopy techniques will be deployed that can quantify the extent of the altered layer (by ^{1}H NMR) and selectively probe and identify the structure of both crystalline and amorphous components present or re-precipitated on the glass surface by ^{1}H- cross polarisation techniques. Isotope techniques (column separation and detailed mass spectrometry) to determine the isotopic ratios in solution as a function of time provide the complementary views of the evolution of both solution and surface during the resumption process.

Profile
The PhD candidate will study in the Mineral Physics group at the Department of Earth Sciences, University of Cambridge. Suitable for Physicists, Chemists, Materials Scientists and Earth Scientists with previous experience of some of the analytical techniques detailed above and previous training in atomistic approaches to understanding complex mechanisms in solids.