PhD Proposal : Nuclear Energy DTC (Cambridge/IC/OU) Feb 2014

# Chemical and Radiolytic Ageing of Actinide Oxides by MAS-NMR

## Project Summary:

**Introduction:** AWE is interested in i) the radiolytic ageing of oxide materials, and ii) the interaction of unaged and aged oxides with hydrogen.

1. Whilst the radiolytic ageing of actinide metals (for example Pu) has received considerable attention, little attention has been paid to the oxides (for example $PuO_2$, $UO_2$, $Pu_2O_3$). It is thought that radiolytic damage will increase in the lattice as a function of time (due to both defects induced by atomic collisions and, possibly, by the in-growth of He) until such time as the annealing out of damage (as a result of radiolytic events) balances the in-growth of damage (as a result of radiolytic events). This project aims to begin to generate knowledge in this area.

2. The sponsor is interested in understanding the location and properties of hydrogen (or deuterium) both within bulk oxides (possibly deposited there by infusion at high temp and pressure) and on the surfaces of oxides (either as hydroxyls or other species). This project is a way to begin to generate knowledge in these areas. The ultimate aim of this type of enquiry would be to understand the nature of the hydrogen at an oxide-gas interface and / or its nature as it dissolves into the oxide lattice.

**Background:** This project intends to utilise MAS-NMR of O-17 (and other multinuclear NMR as appropriate) to probe i) the increase in disorder of an oxide system with time or radiation dose, and ii) utilise 17-O MAS-NMR as an indirect probe of the influence of hydrogen upon oxygen atoms.

**Project Scope:**

A) Cerium oxides ($CeO_2$ and possibly $Ce_2O_3$): Generation of $^{17}O$ oxide powders through a hydride-dehydride-oxidation route.
   a. Radiolytic ageing
      i. Artificial ageing of cerium oxide powders through either high energy atom bombardment (e.g. GANIL) or neutron bombardment of $^{10}B$ added component
      ii. NMR studies to ascertain impact of radiolytic damage on samples (Cambridge)
      iii. High temperature vacuum anneal studies to successively remove damage, followed by NMR (Cambridge)
   b. Chemical ageing by exposure to H
      i. Dosing of cerium oxide powders with H or D at high pressures and temperatures (possibly at sponsor site)
      ii. NMR studies to investigate surface and bulk hydrogen species through various NMR techniques (Cambridge)
      iii. High temperature vacuum anneal studies to successively remove hydrogen species from samples, followed by NMR (Cambridge)

B) Uranium oxides ($UO_2$, $UO_{2+x}$, higher oxides): Use of $UO_2$ samples at Cambridge with labelling of sample surfaces with treatment of $UO_2$ with $H_2{}^{17}O$
   a. Chemical ageing by exposure to H through surface labelling preparation
      i. Study of H/D in near surface layer of sample by NMR (Cambridge)

C) Transactinides (including $AmO_2$, $PuO_2$, $NpO_2$, $UO_2$, $ThO_2$): Samples already exist at ITU but may be reprepared as required.
   a. Radiolytic ageing

i. Proposal to be submitted for the study of $^{17}O$ labelled transactinides. Work will focus on self-irradiation damage on these samples monitored as a function of time (ITU)
ii. If appropriate, additional analyses of these samples by XRD and Raman and an attempt to tie to AWE generated data (ITU)

D) NMR spectroscopy modelling of species using DFT methods (Cambridge)

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