

MAS-NMR of actinide oxide nanoparticles

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Several nations, particularly the UK, house stockpiles of civilian plutonium oxide. With the closure of most fast reactor programmes, these stockpiles are increasingly being seen as liabilities [1]. The long-term chemical and radiolytic aging of stored plutonium dioxide is a serious concern due to the potential production of hydrogen (from adsorbed water) through radiolytic reaction and subsequent chemical or physical incorporation into the oxide. This work uses ceria, thorium and uranium as surrogate fluorite structures. ¹⁷O magic-angle spinning nuclear magnetic resonance (MAS-NMR) of fluorite actinides [2] shows great sensitivity to differences in the local oxygen environments in these oxides and previous work on nano-particles of non-radioactive ceria [3] has demonstrated that ¹⁷O MAS-NMR can be used to distinguish between resonances in bulk ceria and those in the first three atomic layers in the oxide surface.

Prior to NMR experiments, nanoparticle samples are enriched with ¹⁷O by heating in a sealed PTFE lined steel vessel with ¹⁷O enriched water. NMR results indicate a number of peaks corresponding to bulk, surface, sub-surface and defect oxygen environments. The number of NMR peaks produced by ¹⁷O enriched nanoparticles are difficult to assign unequivocally. Theoretical chemical shifts calculated using DFT are used to help assign experimental peaks to specific oxygen environments. In addition, we present a hydrothermal method of producing actinide (and other) oxide nanoparticles with predominant surfaces from selected crystal planes, which simplifies the study and allows confident identification of oxygen environments at oxide surfaces and potentially their response to dosing with hydrogen.

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