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$U_xTh_{1-x}(C_2O_4)_2$ Solid Characterisation Studies

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Abstract

Many advanced reprocessing schemes under development are aimed at co-processing and co-conversion of actinides, unlike current reprocessing plants that produce separate uranium and plutonium products. The most well developed option for the co-conversion stage is probably oxalate co-precipitation, followed by the thermal co-conversion to a mixed oxide product. It is thus envisaged that future processes will avoid separation of plutonium from uranium and instead allow part of the uranium to flow with the plutonium, resulting in co-precipitation as the oxalate, and finally co-conversion to a mixed uranium-plutonium oxide (MOX), which can be fabricated into recycled nuclear fuel for further energy generation.

The co-crystallisation of uranium (IV) and plutonium (III) into a single oxalate structure ensures the homogenous distribution of the two actinides at the molecular scale. The joint conversion of uranium and plutonium to the oxide form makes it possible to remove the complicated step of blending and grinding the two distinct oxide powders, as currently employed for the purposes of MOX fuel fabrication. This concept can also be extended to other actinides, including minor actinides from partitioning processes such as SANEX (Selective Actinide Extraction) and GANEX (Grouped Actinide Extraction) processes or even a thorium containing product from recycle of thorium based fuels.

A selection of $U_xTh_{1-x}(C_2O_4)_2$ solids at varying concentrations of uranium and thorium were prepared by oxalate co-precipitation. Uranium (VI) was conditioned electrochemically at -0.7 V to uranium (IV), in the presence of hydrazine. The reduced uranium (IV) in nitric acid was mixed with thorium nitrate solutions at different concentration ratios with oxalic acid. The mixed tetravalent uranium-thorium oxalate solid products have been characterised by Raman and IR spectroscopies. The influence of thorium substituted into the uranium oxalate structure was evaluated. Several vibrational modes were found to be affected by the variation in ionic radius appearing to be metal sensitive and therefore, provide the initial indication in the evaluation of the chemical composition.

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1. Introduction

Nuclear fuel reprocessing using the PUREX process is well established, with over 60 years experience in diverse countries e.g. UK, France, Japan, US and Russia.¹ Initially developed by Anderson and Asprey at the University of Chicago as part of the Manhattan Project under Glenn T. Seaborg in 1947², the PUREX process rapidly became the process of choice from the 1950s onwards. The process involves dissolution in nitric acid followed by the separation and purification of uranium and plutonium by solvent extraction using tri-butyl phosphate. The PUREX process is a rather complex undertaking, purifying and transforming used nuclear fuel in to solid uranium and plutonium oxide products suitable for manufacture into new fuel.³

Current UK Government policy is to support the delivery of new nuclear builds up to a capacity of 16 GW with the used fuel interim stored before disposal (i.e. a transition to the open fuel cycle once the UK's reprocessing plants close around 2020). Recently, the UK Government published a nuclear energy roadmap that identified a bounding scenario in which up to 75 GW of nuclear energy could be required this century to meet the UK's low carbon energy needs. The bounding scenario is assumed to involve the possible introduction of fast reactors and an advanced closed fuel cycle with reprocessing of spent fuel from light water reactors (LWR) and fast reactors.⁴

Many advanced reprocessing schemes under development are aiming to design improved PUREX-based processes through co-processing and co-conversion of actinides in order to provide additional barriers against perceived risks of nuclear proliferation by avoiding pure plutonium products. For instance, a variant of the PUREX process known as the COEXTM process has been designed by French organisations, CEA and AREVA, where it is envisaged that the process will avoid separation of plutonium from uranium and instead allow part of the uranium to flow with the plutonium, resulting in co-precipitation as the oxalate, and finally co-conversion to a mixed uranium-plutonium oxide (MOX).⁵ The co-crystallisation of uranium (IV) and plutonium (III) into a single oxalate structure ensures the homogenous distribution of the two actinides at the molecular scale.⁶ The joint conversion of uranium and plutonium to the oxide form, as long as uranium is maintained in the tetravalent state, makes it possible to remove the complicated step of blending and grinding the two distinct oxide powders, as currently employed for the purposes of MOX fuel fabrication.³ This concept can also be extended to other actinides, including minor actinides from partitioning processes such as SANEX (Selective Actinide Extraction) and GANEX (Grouped Actinide Extraction) processes or even a thorium containing product from recycle of thorium based fuels. Therefore, co-conversion of actinides to mixed oxide powders, for fabrication into new nuclear fuels for further energy generation, can benefit the proliferation-resistant nature of the reprocessing plant flow sheet, as well as potentially reducing the size and complexity of the recycle plant.

In support of these objectives, an initial series of experiments preparing mixed tetravalent uranium-thorium oxalate compounds by co-precipitation have been completed and the products characterised by Raman and IR spectroscopies. The initial series of experiments enable the redox behaviour of uranium to be studied whilst in the presence of the redox stable thorium (IV) before moving onto more radioactive and redox-active (U,Pu) mixtures. The thorium experiments have additional benefit with regards to the development of the thorium fuel cycle.

The next stage is to calcine these precipitates to produce directly solid-solution (U,Th) mixed oxides, which enables the study of the possible U (IV)-(VI) conversion during calcination. The study enables the investigation of uranium redox behaviour before increasing the complexity of the experiments by addition of other actinides with high specific activities i.e. Th (IV)/Pu (IV), U (IV)/Pu (III) and U (IV)/Am (III).

2. Experimental Section

2.1. Synthesis & UV-Vis Spectroscopic Analysis

A uranium (VI) nitrate solution (0.76 M) was conditioned electrochemically to uranium (IV), in the presence of the chemical stabilizer hydrazine. The electrochemical conditioning equipment consisted of an electrochemical cell with three electrodes; a working electrode, an auxiliary electrode and a reference electrode. The auxiliary electrode comprised of a platinum wire isolated by a glass frit in a 2 M nitric acid solution; contact with the solution was through the glass frit. The working and reference electrodes were reticulated vitreous carbon mesh and Ag/AgCl electrodes, respectively. The uranium (VI) solution was reduced at a constant current using a Solartron Potentiostat, Model 1285, running at 0.7 V at a fixed rate of 0.1 points/sec and under a nitrogen air flow of 80ml/min. The

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