The Development of Zirconolite Glass-Ceramics for the Disposition of Actinide Wastes

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The UK has been reprocessing spent nuclear fuel since the 1950's and has a resultant 140 tonne stockpile of civil separated PuO_2. Whilst the current UK Plutonium Policy is to fabricate the PuO_2 into Mixed Oxide (MOx) fuel, a significant portion of the stockpile material will be unsuitable for fuel fabrication rendering it as future higher activity waste. As such, there is a need for research and development of wasteforms and treatment methods for immobilising these high activity wastes. The UK has a catalogue of Pu-based wastes known as Pu-residues. These wastes are highly heterogeneous and both chemically and physically variable, thus require a flexible wasteform and waste treatment option that can accommodate the wide variations. It is envisaged that a waste immobilisation route suitable for Pu-residues may conform to future requirements for processing other stockpile material identified as waste.

The Nuclear Decommissioning Authority (NDA) has identified hot isostatic pressing (HIPing) as a potential thermal treatment option for consolidating Pu-residues into suitable wasteforms (1). HIPing provides a wide operating window and can process various wasteform materials into dense, hermetically sealed waste packages ready for long-term storage and eventual geological disposal. The flexibility of HIP means low volume, complex waste-streams, such as Pu-residues, can be treated on a case by case basis and ultimately processed on the same plant line into ceramic, glass-ceramic or metal encapsulated wasteforms. Advantages of HIP for processing PuO_2 wastes, such as the civil stockpile material, also include; significant waste volume reductions, excellent Pu accountancy throughout the plant-line and minimal secondary waste production.

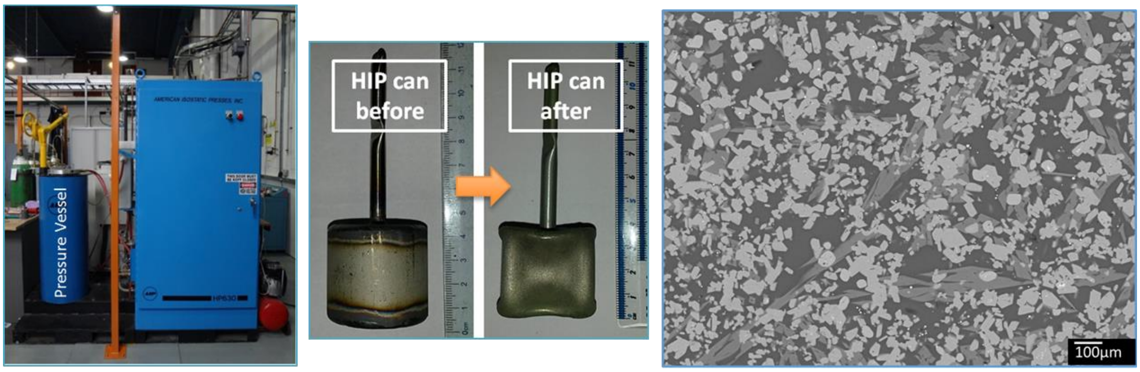

Figure 1: Images of the hot isostatic press (HIP) at The University of Sheffield (Left), an example of a HIP canister before and after processing (Centre), a scanning electron microscopy micrograph of a glass-ceramic microstructure (Right).

This PhD project aimed to develop high fraction zirconolite glass-ceramics for the disposition of Pu-based higher activity wastes within the UK and utilised HIP as the thermal treatment method throughout. Following on from previous work in this area, conducted by the UK's National Nuclear Laboratory (NNL) and the Australian Nuclear Science and Technology Organisation (ANSTO), this thesis studied zirconolite glass-ceramics for Pu disposition, with primary focus on; formulation optimisation, the effect of CaF_2 as a waste digesting agent, the effect of Cl contamination and waste incorporation behaviour through surrogate studies and PuO_2 validation tests.

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Formulation studies revealed a strong correlation between glass composition and the resultant crystalline phase assemblage in the glass-ceramics. An Al_2O_3 rich glass was found to promote a higher yield of zirconolite and subsequently reduced the abundance of accessory phases in the final wasteform. It was hypothesised that changes to the glass structure, with increased levels of Al_2O_3, resulted in a lower solubility of the ceramic forming oxides in the glass phase, thus promoted the formation of zirconolite. Through the formulation studies the stages of phase formation were also investigated and revealed information on intermediate phases and those precipitated from the melt during cooling.

CaF_2 was shown to be an effective waste digestion agent, but was eliminated from the glass-ceramic formulation to reduce the neutron source term of the wasteform. Through formulation investigations and waste incorporation trials, a glass-ceramic formulation and processing route that achieved full waste incorporation and suitable phase assemblages and microstructures, without the need for CaF_2, were achieved. This result meant the neutron source term of the wasteform was reduced by removal of the 100 % abundant ^{19}F ions, which partake in damaging (α,n)-reactions. This was a significant result for the future acceptance of the waste packages for geological disposal by reducing a contributing factor to the risk of criticality.

Some of the PuO_2 materials requiring treatment are contaminated with Cl due to the degradation of PVC (polyvinyl chloride) packaging during storage. The Cl solubility limit of the optimised glass-ceramic formulation was found to be 3 – 4 times higher than the conservative upper limit of contamination expected in the wastes. Contamination levels of this magnitude had no detrimental effects on the microstructure or phase assemblage of the glass-ceramics and did not inhibit CeO_2 incorporation.

Incorporation studies confirmed the preferential incorporation of actinide surrogates into the ceramic phase(s) (2) (3). The reduction of Ce was shown to promote the formation of a Ce-rich perovskite phase. The U study achieved near complete digestion of the UO_2 surrogate, with preferential incorporation into the zirconolite phase. The development of the glass-ceramic system and successful results of the surrogate studies, led to the fabrication and characterisation of PuO_2 bearing HIP samples. These samples were part of a validation study towards investigating the effect of controlled oxygen fugacity on the partitioning behaviour of Pu within the glass-ceramic wasteform. The results in this thesis, confirmed complete incorporation of the PuO_2 and achieved microstructures and phase assemblages that were indicative of those obtained through the surrogate studies.

This work has given a new insight into the mechanisms controlling phase formation and waste incorporation, essential for understanding these glass-ceramic wasteforms. This thesis demonstrates a clear progression from process and formulation optimisation, to surrogate studies and the consolidation of PuO_2 containing HIP samples, with promising and exciting results with regards to the development of the wasteform. A major part of this work focused on surrogate studies but the author was able to validate these results with PuO_2 at the Australian Nuclear Science and Technology Organisation (ANSTO). This was a huge advancement of this research that was unattainable within the UK’s current capabilities. As well as wasteform development, this work has contributed to the advancements of the HIP technology for processing radioactive waste, through the installation of the Active Furnace Isolation Chamber (AFIC) at The University of Sheffield. The results from this project have a direct impact and current relevance to the UK’s Pu management strategy and provides a framework of information that is applicable to the current industrial developments in this area of nuclear waste management.

Since completing her PhD studies, Stephanie has become a senior research technologist within the thermal treatment team of the National Nuclear Laboratory (NNL) and has continued to apply her PhD results, skills and knowledge to ongoing projects developing the HIP technology and ceramic wasteforms for management of the UK's PuO_2. This PhD research is playing a key part in furthering the wider understanding and technology readiness level of this treatment option within the industry and ultimately add value to the NDA's portfolio to advise the UK government on a long-term solution.

References

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