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The development of zirconolite glass-ceramics for the immobilisation of Pu-residues in the UK.

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The UK has over 100 tonnes of separated PuO2 stored at the Sellafield site. The UK policy for managing this plutonium stockpile is to reuse this material as MOx fuel. However, not all of the material is suitable for reuse and a proportion has been classified as higher activity waste. These plutonium wastes, and any material which is not ultimately reused, will require immobilization, in a passively safe wasteform, for long-term storage and eventual geological disposal. One proposed treatment plan is hot isostatic pressing of the plutonium waste / stockpile material, with suitable precursors, to form a glass-ceramic or full ceramic wasteform, inside stainless steel canisters. Glass-ceramic materials are proposed for the low purity and highly variable wastes, in which the glass phase provides wasteform flexibility to accommodate impurities and variations in the waste feed composition. The plutonium partitions into the more durable ceramic phase, zirconolite (CaZrTi2O7). Zirconolite has excellent wasteform properties including durability and radiation tolerance, and readily accepts actinides and rare earths into its crystal structure.

In this work, the formation of zirconolite is shown to depend sensitively on glass fraction and composition, such that an Al rich glass promotes a higher yield of zirconolite. The thermodynamic activity of Si in the system drives the crystalline phase assemblage, by determining whether it is consumed in the amorphous glass phase or undesired accessory crystalline phases, such as sphene (CaTiSiO5) and zircon (ZrSiO4). The design of an optimized glass-ceramic formulation is demonstrated, to maximize the yield of zirconolite and minimise the yield of accessory phases. The partitioning of CeO2, within the glass-ceramic wasteform, as a PuO2 surrogate, was studied using various charge compensation mechanisms, under an imposed Fe/FeO and Ni/NiO buffer. Analysis by SEM/EDX, XRD, and Ce L3 edge XANES, demonstrated reduction of Ce(IV) to Ce(III) to favour incorporation of Ce within a perovskite accessory phase and the glass matrix. Ce partitioning in the zirconolite phase was maximized when retained as Ce(IV). These results demonstrate a feasible wasteform formulation for disposition of UK plutonium wastes and stockpile material.

Summary

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