THE EFFECT OF INTERFACIAL MATERIAL ON TAILORED CERAMIC NUCLEAR WASTE FORM DISSOLUTION

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The long radioactive lifetime of the fission products in nuclear wastes requires that the material be isolated from the biosphere for periods of $10^3$ to $10^5$ years. One method of accomplishing this is to consolidate the waste into a chemically stable solid form contained within a multiple barrier canister which can be transported to a geologically stable repository for long-term storage. A number of candidate solid waste forms are being assessed to determine their suitability for incorporating various nuclear waste compositions. These include the current reference form (borosilicate glass), ceramics, high silica glasses, and cementitious forms. In this laboratory, research is currently being conducted on chemically immobilizing synthetic nuclear waste in high alumina content tailored ceramics, made by high temperature and pressure consolidation of the waste material with selected additives to produce a fully dense, fine grain ceramic. The specific crystalline phase assemblages produced by tailoring the waste sludge provides chemical host sites for the individual radionuclides in ceramic phases which closely approximate natural mineral assemblages that have proven stability over geologic time scales.

The high alumina content tailored ceramics are composed of the compatible crystalline species iron-manganese spinel [nominally $(\text{Mn,Fe})\text{Al}_2\text{O}_4$], magnetoplumbite [nominally $X(\text{Al,Fe,Ti})_2\text{O}_19$, where $X = \text{Sr, Ba, Cs}_{0.5} + \text{La}_{0.5}$, etc.] and a cubic $(\text{U,Zr,Th})\text{O}_2$ uraninite phase. The presence of an excess of any of the tailoring additives, Al, RE (rare earth) or Ti over that required to form the radiophases produces one compatible additional phase: $\text{Al}_2\text{O}_3$ (corundum) when Al is in excess, rare earth perovskite, $\text{RE} (\text{Al,Fe})\text{O}_3$, when rare earth is in excess, and pseudobrookite,
(Fe,Ti,Al)$_2$TiO$_5$, when Ti is in excess. These phase assemblages produce ceramic waste forms which have a low surface area and are extremely hard and dense.

In evaluating the tailored ceramics for comparison with other waste forms, one of the major criteria for assessing performance is the resistance of the form to dissolution when in contact with ground water at the elevated temperatures (up to 100°C) in the vicinity of the waste monolith. Such dissolution or "leach" resistance is the ultimate barrier in preventing radionuclide release into the biosphere. In a multiphase ceramic there are a number of physical and chemical effects contributing to the ability of the form to immobilize radionuclides when in contact with water. These include the solubility of the individual phases, the degree to which the radionuclide host phases are microstructurally isolated or encapsulated by inert phases, the absence of intergranular amorphous material, and the formation of passivating surface layers during the dissolution process.

In this study the role of chemistry and microstructure, in particular the presence of intergranular glassy phases, on the overall dissolution process are explored. Two samples, one Al and Ti tailored which contained appreciable glass and the other Al and RE tailored which contained little or no intergranular phase, are used to illustrate the effect of microstructure and provide an assessment of the waste form's long term stability.

Experimental

The specific waste composition used in this study is a simulated "composite," representative of the high level defense nuclear waste currently being stored at the Savannah River Nuclear Waste Repository. Though actual SR wastes are highly variable from tank to tank, the "composite" composition shown in Table 1 does give a representation of the major waste elements. The ion-sieve listed is an additive used in the collection of soluble Cs from the liquid fraction of the waste. The major elements of concern with respect to release into ground water are the radioisotopes of Cs, Sr, Th, U, Pu, rare earths and actinides. In this study only cold isotopes were used except for depleted Th and U, with the transuranics being simulated crystal chemically by rare earths.

The starting powders for the ceramics were prepared as dried hydroxides by either co-precipitation or spray drying of nitrate solutions. The hydroxides were ground, calcined to 800°C, and then ball-milled to produce a highly reactive powder for consolidation. The consolidation was carried out by reactive hot pressing at temperatures from 1200 to 1300°C at 4000 psi for 1 hr in 1 in. diameter graphite dies. Al(OH)$_3$ powder was used to surround