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Solubility study of Ti,Zr-based ceramics designed to immobilize long-lived radionuclides

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ABSTRACT

Aqueous alteration of five Ti-Zr-oxide-based ceramics containing elements simulating long-lived radionuclides was studied experimentally by leaching at 90 °C in deionized water for more than one year under conditions of high solid/liquid ratios. Four of these ceramics were synthesized by cold-crucible melting (two Synroc-like materials, one zirconia, and one aluminotitanate) and the fifth ceramic was a hot-pressed Synroc. Melted Synroc-like ceramics have the same major constitutive phases as hot-pressed Synroc, but crystal sizes are very different, millimetric as opposed to micrometric, respectively.

After the first seven days of leaching, the alteration appeared to cease as solution concentrations for all of the constituent elements attained constant values. The altered mass percentages determined from the release of Ca and Mo were less than 0.2% of the initial mass. Thermodynamic equilibrium calculations using data or estimations for pure phases, or using a model of ideal solid solutions, showed that the cessation of the alteration cannot be explained by the solubility limit of the primary phases of these ceramics. But, the data could be interpreted by the development of a passivating layer of secondary phases, e.g., hydroxides. Examination of the altered surfaces was carried out using SEM, XRD and XPS; however, the thickness of the alteration layer, estimated as 3–5 nm, was below the resolution limit of these techniques. Finally, despite the differences in the crystal size and therefore the amount of grain boundaries, and in the synthesis redox conditions, the leaching behaviors of melted and hot-pressed Synroc are the same for the present experiments.