Dissolution kinetics of pyrochlore ceramics for the disposition of plutonium

Pacific Northwest National Laboratory, P.O. Box 999 (K6-24), Richland, Washington 99352, U.S.A.

Abstract

Single-pass flow-through (SPFT) experiments were conducted on a set of non-radioactive Ti-based ceramics at 90 °C and pH = 2 to 12. The specimens contained 27.9 to 35.8 wt% CeO₂ as a surrogate for UO₂ and PuO₂. Compositions were formulated as TiO₂-saturated pyrochlore (CeP₁) and pyrochlore-rich baseline (CePB₁) ceramic waste forms. Pyrochlore + Hf-rutile and pyrochlore + perovskite + Hf-rutile constituted the major phases in the CeP₁ and CePB₁ ceramics, respectively. Results from dissolution experiments between pH = 2 to 12 indicate a shallow pH-dependence with an ill-defined minimum. Element release rates determined from experiments over a range of sample surface areas (S) and flow rates (q) indicate that dissolution rates become independent of q/S values at 10⁻⁴ to 10⁻⁷ m/s. Dissolution rates dropped sharply at lower values of q/S, indicating that rates are subject to solution saturation effects as dissolved constituents become concentrated. Forward dissolution rates were 1.3(0.30) × 10⁻³ and 5.5(1.3) × 10⁻³ g/m²·d for CeP₁ and CePB₁ ceramics, respectively. Dissolution rates obtained in other laboratories compare well to the findings of this study, once the rate data are placed in the context of solution saturation state. These results make progress toward an evaluation of CeO₂ as a surrogate for UO₂ and PuO₂ as well as establishing a baseline for comparison with radiation-damaged specimens.

Keywords: Crystal structure, radiation damage, kinetics, dissolution rate, phase transition, amorphization, XRD data

Introduction

Research on Ti-based ceramics as an immobilization form for Pu has been carried out at several international organizations (ANSTO 1999; Bakel et al. 2000; Burakov and Anderson 2001; Ebbinghaus et al. 1999; Hart et al. 2000a; Kuramoto et al. 1998; Leturq et al. 2001; McGrail et al. 2001; Ringwood 1978; Vance et al. 1996; Volokov et al. 2001). In the United States, research on these ceramic materials was spurred by the negotiations between Russia and the United States over the disposition of weapons-grade Pu declared excess. Under the initial framework of the treaty, the United States pursued a dual strategy of incorporating the Pu as PuO₂ into mixed oxide fuel that can be “burned” in a commercial reactor and some less suitable material containing Pu to be disposed of in an in-ground repository at Yucca Mountain, NV (DOE 2002). In this second scenario, the Pu was to be converted to a pyrochlore-based polycrystalline ceramic that would be approximately 25 mm high and 70 mm in diameter. Several of these ceramic disks would be placed in stainless steel cans that would be hung on a rack inside of a high-level waste canister that would subsequently be filled with high-activity radioactive glass (Myers et al. 1998). Under model conditions, the only crystalline phase in the Pu immobilization form would be pyrochlore (ideally Ca₂(U,Pu)₂O₇). However, the Pu feed from various sources has impurities that result in crystallization of other phases. Thus, the baseline formulation for the ceramic would contain pyrochlore as the dominant phase with zirconolite, brannerite, and rutile in various proportions. In the final treaty, the immobilization option was discarded (DOE 2002). Although the development of the immobilization process was stopped, the radiation-damage studies in which these dissolution experiments were performed were continued (Strachan et al. submitted).

Under the immobilization option, an important consideration was prevention of nuclear criticality, which could occur as the waste form underwent corrosion. Because the formulation included neutron absorbers, such as Gd and Hf, in adequate concentrations, the Pu immobilization form was critically safe when stored in an infinite array with full moderation from water (TRW 1997, 2000). To assure the public and the regulators that materials at Yucca Mountain are stored safely, a total system performance assessment was undertaken. As part of this performance assessment exercise, certain assumptions were made about the ceramic Pu immobilization form (TRW 1997). If the fully radiation-damaged ceramic were not to perform as predicted, the ceramic would probably not be acceptable for immobilization of weapons-grade Pu. Thus, a decision was made at the U.S. Department of Energy (DOE) to continue the radiation-damage experiments, which included the dissolution experiments reported here, so that a full package of data would be available to support any future decision on the use of a Ti-based immobilization form.

Studies of natural Ti-bearing phases indicate slow aqueous corrosion rates (Ewing and Headley 1983; Lumpkin 2001; Lumpkin and Ewing 1995; Lumpkin et al. 1986, 1988, 2000), but dissolution experiments are needed to quantify fully their chemical durability. Several dissolution rate studies of titanate ceramics have been reported in the literature (Bakel et al. 2000; Begg et al. 2001; Crawford et al. 1999; Hart et al. 2000a, 2000b;