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Dissolution of Plutonium Dioxide using HCl-HF

L. A. Bray
J. L. Ryan
E. J. Wheelwright

October 1986

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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SUMMARY

High-fired PuO_2 (950° to 1700°C) can be dissolved in boiling 6.1 M HCl when the fluoride ion concentration to plutonium mole (F^-/Pu) ratio is >0.5. The amount of PuO_2 (950°C calcined oxide) dissolved in 1 hour increased from ~0.2% to 66%, 91%, and 100% as the F^-/Pu ratio increased from 0 to 0.5, 1.0, and 1.8, respectively. The PuO_2 dissolution rates in HCl-CaF_2 solutions decrease with increasing oxide calcination temperatures and decreasing oxide surface areas. At a F^-/Pu ratio of 1.8, the 1700°C calcined oxide was completely dissolved in 2.5 hours versus 1 hour for the 950°C calcined oxide.

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INTRODUCTION

At the request of Rockwell Hanford Operations, Pacific Northwest Laboratory (PNL) has completed a preliminary study to determine 1) if plutonium dioxide (PuO_2) can be satisfactorily and completely dissolved in constant boiling (6.1 M) hydrochloric acid (HCl), and (2) the dissolution rates for oxides of known surface area. A method for dissolution of PuO_2 in HCl is desired in order to dissolve scrap PuO_2 in a plutonium recovery process designed principally to support pyrochemical processing of chloride salts. This recovery process is based on chloride anion exchange of the plutonium.

Several methods have been studied for the dissolution of PuO_2. The most common method was the use of nitric acid containing a small concentration of fluoride usually added as HF. Cleveland (1970), Ryan and Bray (1980) have reviewed dissolution methods up to about 1980. Aqueous methods, other than HNO_3-HF, included the use of acids such as HI, HBr, and HCl containing $SnCl_2$ (Cleveland 1964; Molen 1967). Refractory PuO_2 dissolves extremely slowly in mineral acids; rates decrease as the calcination temperature of the oxide increases (Bjorklund and Staritzky 1954; Baehr and Dippel 1967). No dissolution data are known for mixtures of HCl-HF.

EXPERIMENTAL PROCEDURE

This section details the preparation of plutonium dioxide, the dissolution procedure, and the equipment used in these tests.

PREPARATION OF PLUTONIUM DIOXIDE

Plutonium dioxide intended for use in the dissolution tests was specially prepared and characterized. Plutonium solutions from nitric acid-anion exchange purification were adjusted to 0.05 M in hydrazine to destroy nitrite ions; ascorbic acid was added to reduce the plutonium to plutonium (III); and oxalic acid was added to precipitate plutonium (III) oxalate. The filtered oxalate was dried and divided into three batches that were calcined for 2 hours in air in alumina crucibles at 350°C, 500°C, or 950°C. Part of the 950°C batch was recalcined in a zirconia crucible at 1700°C in water-saturated 92% Ar-8% H_2 to provide highly sintered oxide. The 350°C calcined oxide had a surface area of 48.7 m^2/g; the 500°C oxide, 39.4 m^2/g; the 950°C oxide, 1.5 m^2/g; and the 1700°C oxide, 0.54 m^2/g, as determined by a modified BET method. The importance of this difference in the surface areas of the four oxide batches is evident from the dissolution tests.

DISSOLUTION TESTS USING HCl OR HCl-CaF_2

Samples of each of the four batches of oxide were dissolved in constant boiling HCl (6.1 M) or HCl containing known amounts of CaF_2. The tests were conducted in a standard narrow mouth (Ⅎ24/40 joint) Erlenmeyer flask. The flask was fitted with a condenser with a Ⅎ24/40 inner joint at the bottom. Condenser water was cooled to 6°C with a temperature bath. The dissolver was heated on a stirring hot plate, and the solution was mixed by a Teflon®-coated magnetic bar. The solution was heated to intended dissolution temperature, then a measured amount of oxide was added to avoid a heatup cycle. Samples were withdrawn and filtered at appointed time intervals, and plutonium content in the aqueous phase was determined.

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RESULTS

Rates of dissolution for the various experimental conditions used in this study are shown in Figure 1. In the absence of fluoride, high-fired PuO_2 (>950°C) was practically insoluble in boiling (6.1 M) HCl, and lower-fired oxide dissolved very slowly. The dissolution rates in pure HCl decrease markedly with increasing calcination temperature of the oxide. The amount of oxide dissolved in 5 hours was 28%, 7%, and ~0.2% for 350°C, 500°C, and 950°C calcined oxide, respectively (the same order as the measured PuO_2 surface areas). An exact correlation with surface area was not observed or expected since 350°C calcined Pu(III) oxalate is probably not completely converted to PuO_2 (Cleveland 1970). In addition, all surface areas measured by the BET gas absorption method may not be readily available for aqueous dissolution. The results at 950°C are similar to those found by Cleveland (1964). Cleveland found that only 0.74% of the initial PuO_2 dissolved after 1 hour. The PuO_2 had been prepared by burning metal in air, and 10 g of the oxide had been treated with 100 mL of boiling 12 M HCl.

With fluoride added to the dissolvent, the rate of PuO_2 dissolution increased significantly as the fluoride to plutonium mole (F^-/Pu) ratio increased from 0 to 2. For 950°C calcined oxide, the amount of PuO_2 dissolved in the first hour increased from ~0.2% to 66%, 91%, and 100% as the F^-/Pu ratio increased from 0 to 0.5, 1.0, and 1.8, respectively. As shown in Figure 1, the dissolution rate in HCl-CaF_2 solutions decreases with an increase in oxide calcination temperature and a corresponding decrease in oxide surface area. At a F^-/Pu ratio of 1.0, only 35% of the 1700°C calcined oxide dissolved in 1 hour versus 91% for the 950°C calcined oxide. At a F^-/Pu ratio of 1.8, complete dissolution of the 1700°C calcined oxide required 2.5 hours versus 1 hour for the 950°C calcined oxide. Acceptable dissolution rates for PuO_2 can be obtained in HCl solutions containing F^- in a ratio to Pu of about 2. Fluoride interferes with HCl Pu(IV) anion exchange, but the addition of Al^{3+} ion after dissolution to complex the F^- ion will counteract this effect.

No studies were performed to determine the effect of other metallic impurities on the dissolution rate of PuO_2 in HCl-CaF_2 solutions.

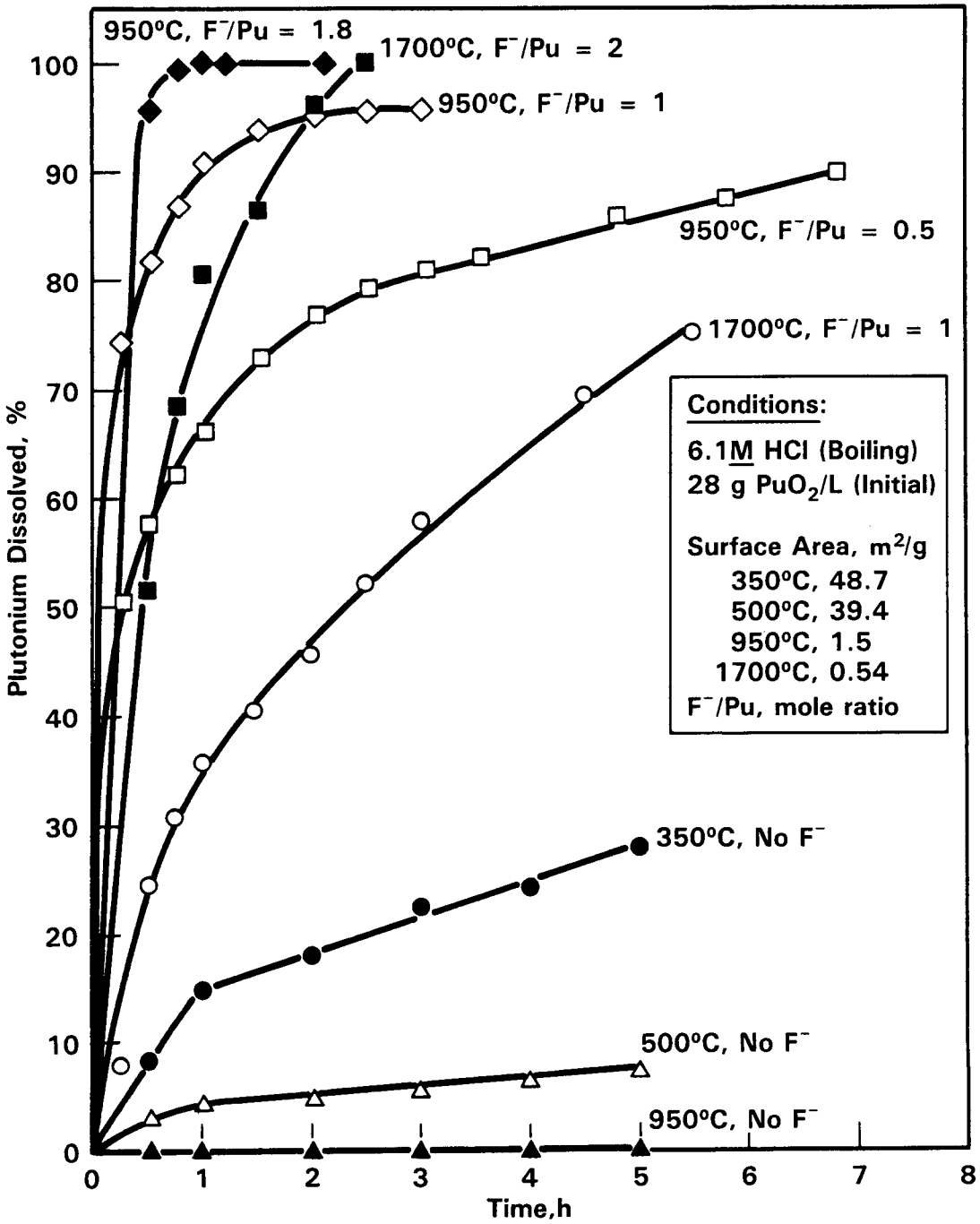

FIGURE 1. Dissolution of PuO_2 Using HCl and CaF_2

Metallic impurities which complex fluoride strongly may be present in quantities approaching total fluoride concentration. Extrapolation from the nitric acid-fluoride system indicates that these impurities will markedly influence PuO_2 dissolution by lowering free F^- and HF activities (Ryan and Bray 1980). Assuming that at any given acidity the PuO_2 dissolution rate is first order with respect to free (uncomplexed to metal) fluoride or HF concentration, the effects of various fluoride complexing metal ions at 25°C can be estimated from their complex formation constants (Sillen and Martell 1964).

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