66 3039

DP-1383

EVALUATION OF FLUORIDE, CERIUM(IV), AND CERIUM(IV)-FLUORIDE MIXTURES AS DISSOLUTION PROMOTERS FOR PuO_2 SCRAP RECOVERY PROCESSES

H. D. HARMON

REG. U. S. PAT. OFF.

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, S. C. 29801

PREPARED FOR THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT AT(07-2)-1

Printed in the United States of America

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

Price: Printed Copy $4.00; Microfiche $2.25

663039

DP-1383
Distribution Category UC-4

EVALUATION OF FLUORIDE, CERIUM(IV), AND CERIUM(IV)-FLUORIDE MIXTURES AS DISSOLUTION PROMOTERS FOR PuO_2 SCRAP RECOVERY PROCESSES

by

H. D. HARMON

Approved by
W. H. Hale, Jr., Research Manager
Separations Chemistry Division

Publication Date - October 1975

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, S. C. 29801

PREPARED FOR THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT AT(07-2)-1

ABSTRACT

Fluoride, cerium(IV), and cerium(IV)-fluoride mixtures were evaluated as promoters for nitric acid dissolution of unirradiated PuO_2 scrap. Fluoride was most effective in promoting rapid and complete dissolution of 80 to 160 g of PuO_2/liter of dissolvent. Cerium(IV) was unsuitable at the high PuO_2/dissolvent ratios normally used in scrap processing because high Ce(IV) concentrations or a Ce(IV) regeneration process were required. Mixing Ce(IV) and fluoride at a ratio of 4 KF/Ce(IV) in 8M HNO_3 increased the PuO_2 dissolution rate at PuO_2 concentrations of less than 10 g/liter, but not at the desired high PuO_2/dissolvent ratios. The dissolution rate of PuO_2 scrap in HNO_3-F^- and HNO_3-Ce(IV) solutions was related inversely to the temperature of the PuO_2 fabrication process.

CONTENTS

LIST OF TABLES AND FIGURES

EVALUATION OF FLUORIDE, CERIUM(IV), AND CERIUM(IV)-FLUORIDE MIXTURES AS DISSOLUTION PROMOTERS FOR PuO_2 SCRAP RECOVERY PROCESSES

INTRODUCTION

Purified plutonium is recovered from assorted PuO_2-containing scrap materials at the Savannah River Plant (SRP) by a process that includes dissolution of the scrap in nitric acid containing fluoride ions, with subsequent solvent extraction and/or ion-exchange purification. A recent Savannah River Laboratory (SRL) study of the nitric acid dissolution of refractory, unirradiated PuO_2 compared fluoride and cerium(IV) as dissolution promoters.[1] Previous studies[2] at Oak Ridge National Laboratory (ORNL) with irradiated UO_2-PuO_2 fuel had demonstrated that fission product ruthenium interferes with PuO_2 dissolution in HNO_3-Ce(IV) solutions. Therefore, the SRL study suggested that nitric acid solutions containing Ce(IV) and Ce(IV)-F mixtures would be most useful for dissolving unirradiated PuO_2 and UO_2-PuO_2 materials such as scrap. The present work was conducted to evaluate and compare such solutions with HNO_3-F^- solutions for dissolution of typical PuO_2 scrap materials and to determine the effect of PuO_2 fabrication history on its dissolution.

EXPERIMENTAL

DISSOLUTION PROCEDURE

Dissolution experiments were conducted with PuO_2 sintered at 1500°C [designated as PuO_2 (1500°C) hereafter], using procedures and equipment described in the previous study.[1] The procedure was modified as follows for Mark 40 and Rocky Flats PuO_2 (described below) to be consistent with present SRP scrap recovery processes:

- Larger PuO_2/dissolvent ratios (80 to 160 g of PuO_2/liter of dissolvent) were used.
- The temperature was maintained at slightly below the boiling point of the dissolvent, generally above 100°C.
- No agitation was provided.

All analyses were performed as described previously.[1]

MATERIALS

Samples of PuO_2 with widely differing properties were chosen for dissolution studies:

- Scrap PuO_2 from Rocky Flats was chosen as an example of an oxide that is resistant to dissolution. Rocky Flats oxide is produced by burning plutonium metal scrap; the metal ignites at about 400°C, and some material reaches 800 to 1100°C. The oxide produced contains less than 3% of free plutonium metal, and 3 to 5 wt % of the oxide is refractory (extremely difficult to dissolve).
- PuO_2 from aged Mark 40 targets (containing approximately 51 wt % ^{242}Pu and hereafter referred to as Mark 40 PuO_2) was selected as a typical nonrefractory oxide. This material is produced from Pu(III) oxalate by calcination to the oxide at 600°C and contains about 0.1% by weight ^{241}Am from decay of ^{241}Pu.
- PuO_2 (1500°C) was prepared as described previously.[1]

All other chemicals used were reagent grade.

RESULTS AND DISCUSSION

DISSOLUTION IN HNO_3-KF SOLUTIONS

The effects of fluoride ion and nitric acid concentrations on dissolution of Rocky Flats PuO_2 and Mark 40 PuO_2 are shown in Figure 1 and Figure 2, respectively. For nearly complete dissolution of Rocky Flats PuO_2, 15M HNO_3-0.2M KF was required; a residue containing plutonium, silicon, and various trace metals remained undissolved in all experiments. For the nonrefractory Mark 40 PuO_2, much lower fluoride ion concentrations gave rapid and complete dissolution, with 0.05M being the maximum KF concentration needed. Comparison of Mark 40 PuO_2 dissolutions in 15M HNO_3-0.025M KF at 80 and 160 g of PuO_2/liter of dissolvent showed that less total fluoride ion was required for complete dissolution at lower PuO_2/dissolvent ratios. Also, nitric acid concentrations lower than 15M were shown to be effective at lower PuO_2/dissolvent ratios.

DISSOLUTION IN HNO_3-Ce(IV) SOLUTIONS

Dissolutions of Rocky Flats oxide in HNO_3-Ce(IV) were conducted with concentrations (80 g of PuO_2/liter of dissolvent)

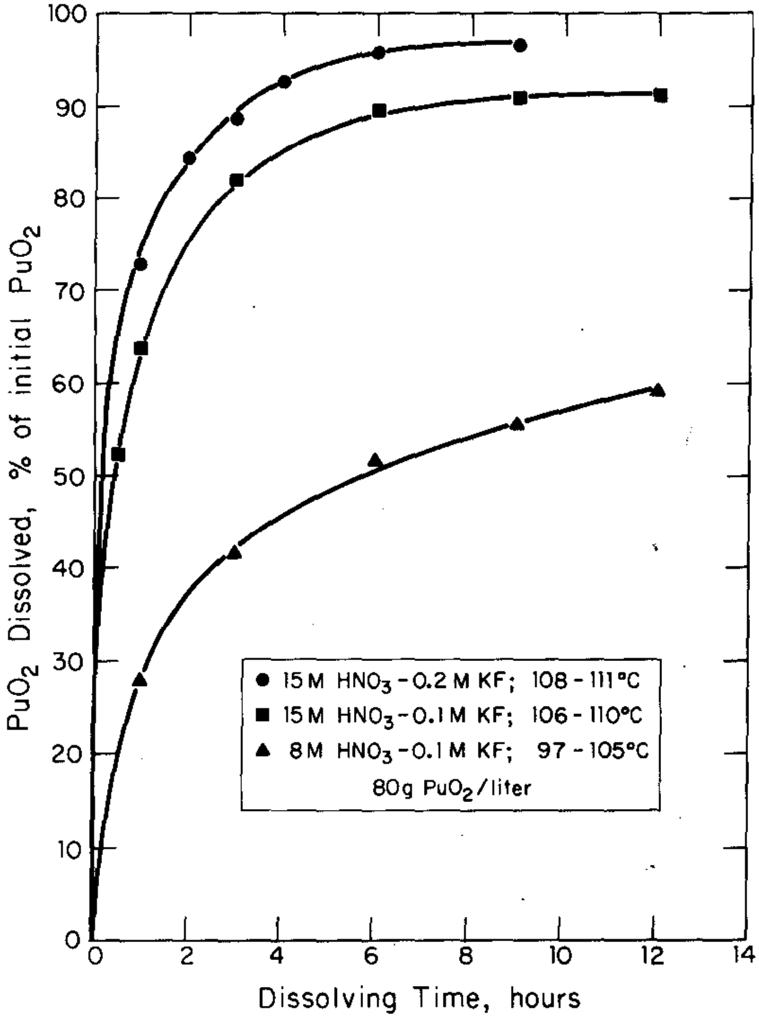

FIGURE 1. Dissolution of Rocky Flats PuO$_2$ in HNO$_3$-KF Solutions

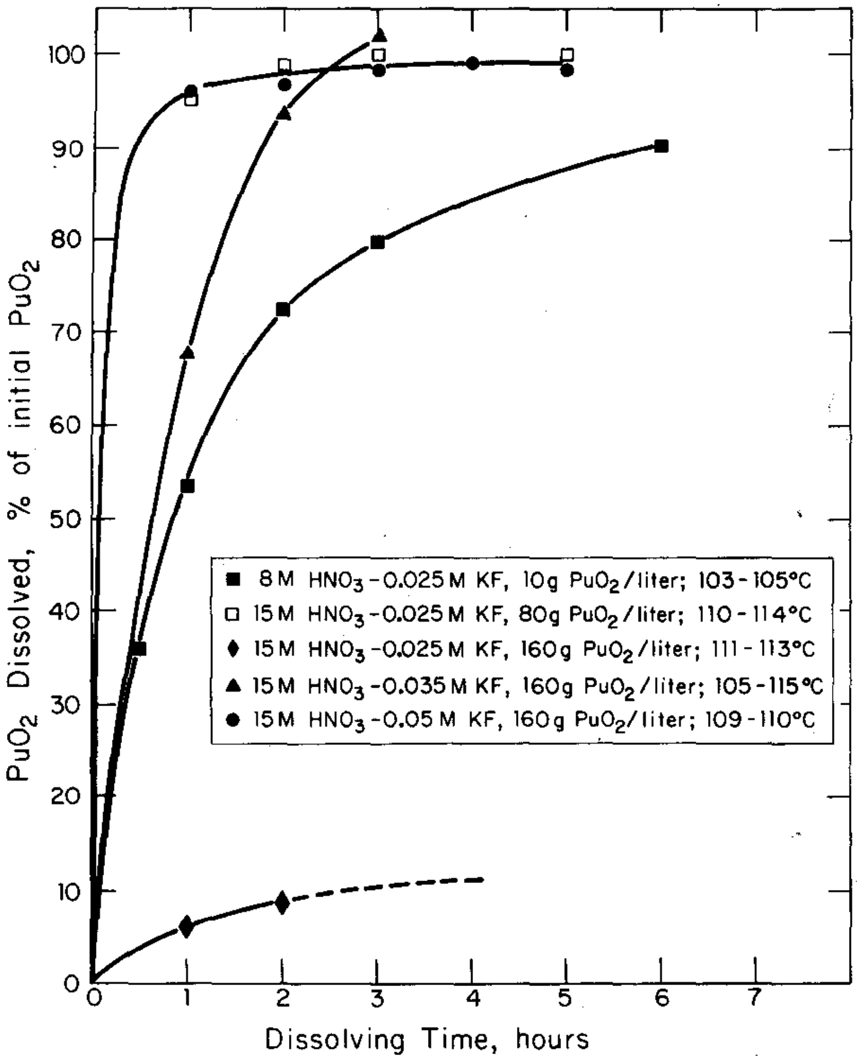

FIGURE 2. Dissolution of Mark 40 PuO$_2$ in HNO$_3$-KF Solutions

approaching the concentrations in current SRP processing. The Ce(IV) concentration was rapidly depleted as shown (Figure 3) by the slow dissolution rate after 1 to 3 hours and by observing the fading Ce(IV) color. Additional Ce(IV) was required to continue dissolution; but in both experiments, dissolution stopped with excess Ce(IV) present. These results agree with ORNL studies[3] which concluded that the Ce(IV)/Ce(III) ratio controls the dissolution rate. Due to the implied requirements of a high Ce(IV)/Ce(III) ratio or a Ce(IV) regeneration process, Ce(IV) seems unsuitable as a dissolution promoter in scrap recovery.

Similar dissolution experiments were conducted with Mark 40 PuO_2; even with this nonrefractory oxide and a smaller PuO_2/ dissolvent ratio, complete dissolution was not attained (Figure 4). The higher dissolution rate attained in 4M HNO_3 is consistent with results of previous studies at SRL[2] and ORNL.[4] In contrast to the results with Rocky Flats oxide, almost all Ce(IV) was consumed in the 4M HNO_3-0.025M Ce(IV) dissolution. Complete dissolution might have occurred if a stoichiometric amount of Ce(IV) had been present, i.e., that concentration of Ce(IV) necessary to oxidize all Pu(IV) to Pu(VI).[1] Even so, dissolution to such low plutonium concentrations (less than 10 g of PuO_2/liter of dissolvent) is impractical for scrap recovery unless future special processing requirements prohibit the presence of fluoride ion.

DISSOLUTION IN HNO_3-Ce(IV)-KF SOLUTIONS

Dissolution rates for Rocky Flats PuO_2 and Mark 40 PuO_2 in two different HNO_3-Ce(IV)-KF solutions are shown in Figure 5 and Figure 6, respectively. The 8M and 15M HNO_3 dissolvent solutions contained fluoride and Ce(IV) ions at a ratio of 4 KF/Ce(IV). With 80 g of PuO_2 per liter of dissolvent, the dissolution rate for Rocky Flats PuO_2 was slightly less than in similar strength nitric acid solutions containing only fluoride ions (Figure 5). In contrast, the dissolution rate for Mark 40 PuO_2 at 10 g of PuO_2/liter of dissolvent containing 4 KF/Ce(IV) was greater than than that for dissolvent containing only fluoride ions (Figure 6). Dissolvent containing the 4KF/Ce(IV) ratio also was effective in improving dissolution of high-fired (sintered at 1500°C) PuO_2 at 7 g of PuO_2/liter of dissolvent.[1] These results indicate that the beneficial effect of mixing Ce(IV) and fluoride ion decreases with increasing PuO_2/dissolvent ratios. This effect may be explained by complexing reactions. Thus, Pu(IV) strongly complexes fluoride ion and, in high Pu(IV) concentrations, the dissolution rate decreases because of the subsequent decrease in the free fluoride ion concentration. Adding Ce(IV) to such a system further decreases the free fluoride ion concentration, and the promoting action of the Ce(IV) apparently does not compensate for this.

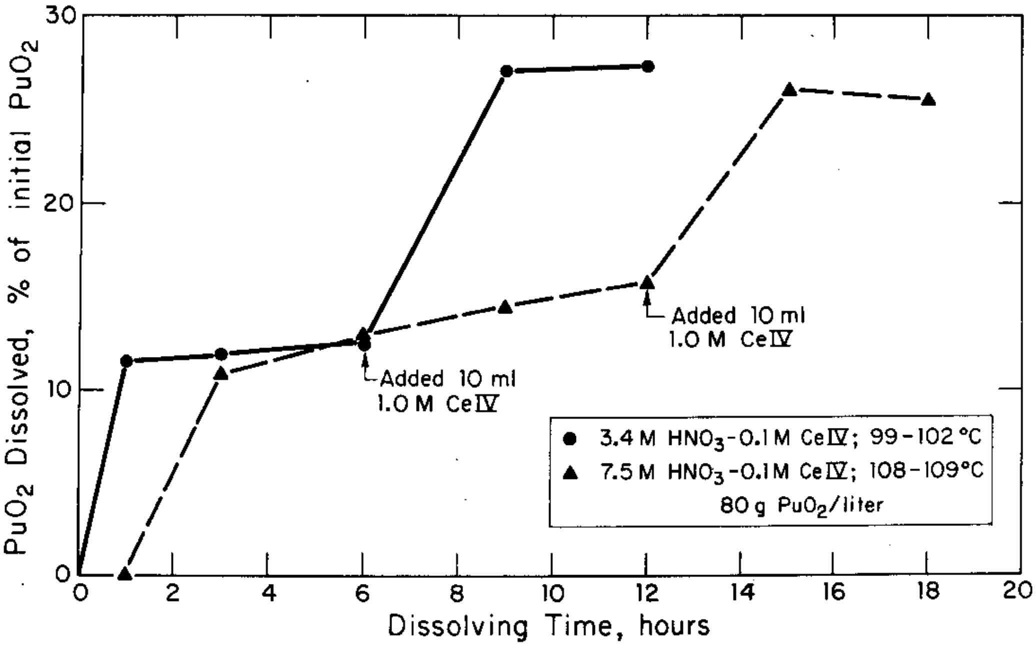

FIGURE 3. Dissolution of Rocky Flats PuO$_2$ in HNO$_3$-Ce(IV) Solutions

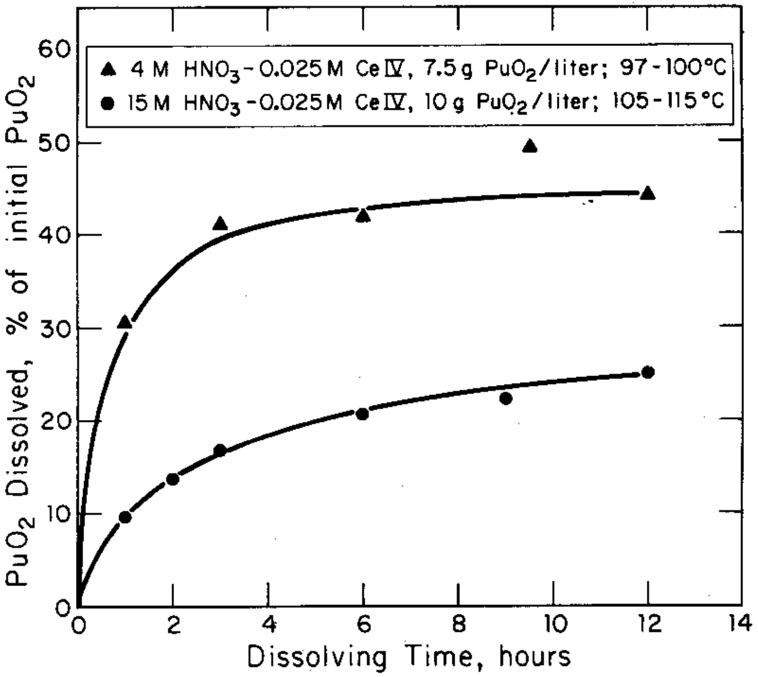

FIGURE 4. Dissolution of Mark 40 PuO$_2$ in HNO$_3$-Ce(IV) Solutions

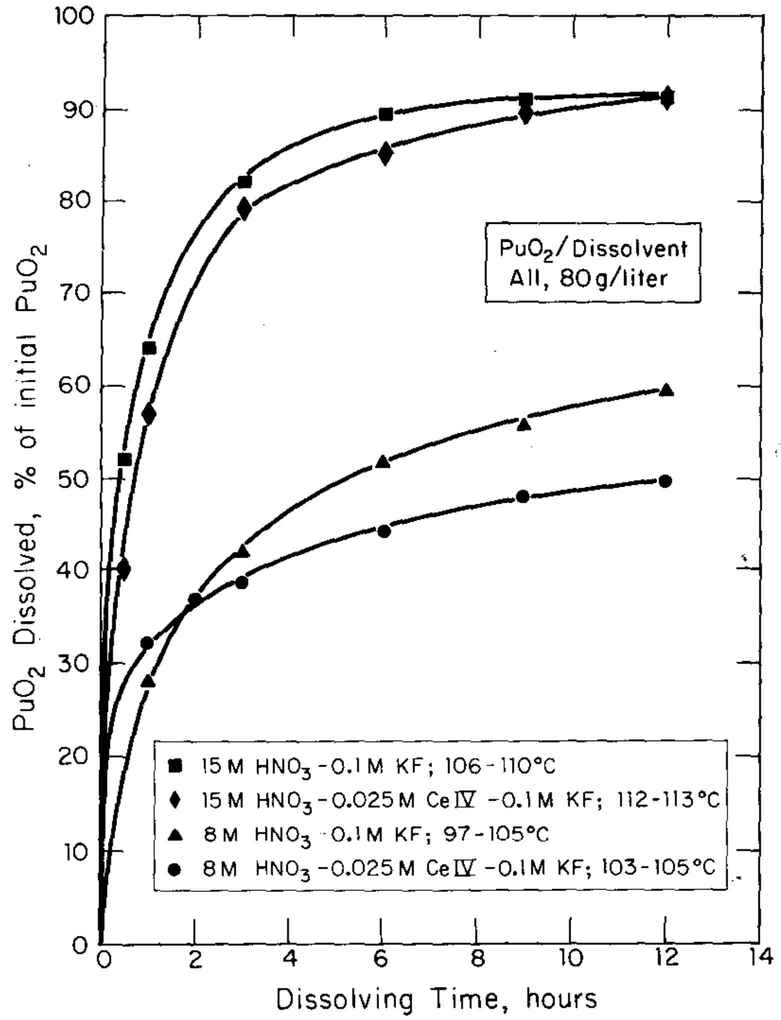

FIGURE 5. Effect of Ce(IV) on Dissolution of Rocky Flats PuO_2 in HNO_3-KF Solutions

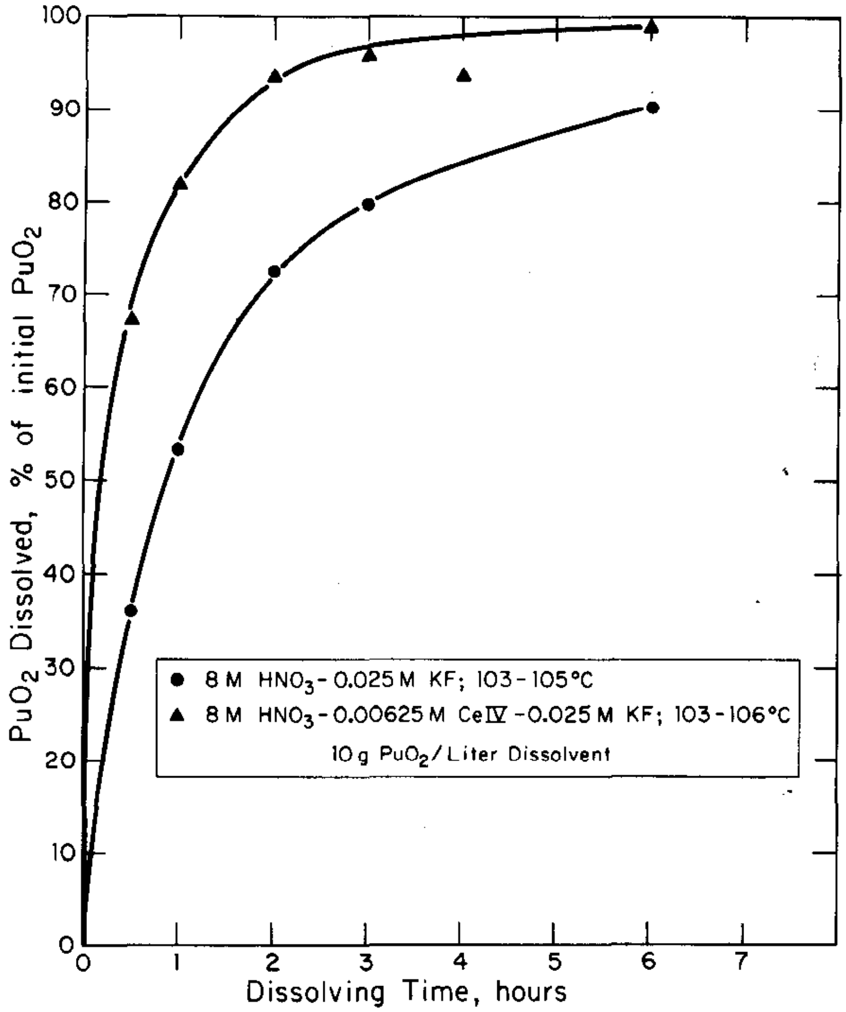

FIGURE 6. Effect of Ce(IV) on Dissolution of Mark 40 PuO_2 in HNO_3-KF Solutions

EFFECT OF THE PuO_2 PREPARATION PROCESS ON DISSOLUTION PROPERTIES

The dissolubility of PuO_2 is influenced by the nature of the starting material, the maximum temperature to which the material has been subjected, and the time at that temperature.[5,6] As the temperature is increased, changes in density and surface area (physical properties which affect dissolubility) result from perfection of the PuO_2 crystal lattice.[5,7,8] Temperatures experienced during preparation of the oxides used in this study are summarized in Table 1.

TABLE 1

Summary of PuO_2 Preparation Processes

	Mark 40 PuO_2	*Rocky Flats PuO_2*[a]	*PuO_2 (1500°C)*	*Microspheres*[b]
Fabrication Method:	Calcination of Pu(III) oxalate	Burning of Pu metal scrap	Calcination of Pu(III) oxalate	Sol gel
Calcination temperature, °C	600	None; Pu ignites at ~400°C; some material reaches 800 to 1100°C	700	800[c]
Calcination time, hr:	3	-	2	2
Sintering temperature, °C:	-	-	1500	1150
Sintering time, hr:	-	-	4	4

---

[a] E. Vejvoda, private communication, Dow Chemical Company, Rocky Flats Division, Golden, Colorado, November 10, 1974.

[b] D. E. Horner, private communication, Oak Ridge National Laboratory, Oak Ridge, Tennessee, January 10, 1975.

[c] Prior to the final calcination, the microspheres are steam dried at 150 to 200°C followed by 1-hour heating periods at 250 and 400°C. The drying steps are followed by steam calcination at 1150°C.

Sufficient data are available from this work and previous studies[1, 4, 8–12] to determine the effect of the different PuO_2 preparation processes on the efficiency of fluoride ion and Ce(IV) dissolution promoters. However, a plot of percent PuO_2 dissolved versus time does not yield a direct comparison between the oxides because of different PuO_2/dissolvent ratios. An alternative method of comparing dissolution data (obtained in experiments of different dissolvent volumes, fluoride ion or Ce(IV) concentrations, and quantities of PuO_2) is to compare the percentage of PuO_2 dissolved (per unit time) based on the initial F^-/PuO_2 or $Ce(IV)/PuO_2$ ratio. This technique was used effectively by Etter and Herald[12] to illustrate the effect of calcination temperature and HF concentration on the dissolving characteristics of $^{238}PuO_2$. For such comparisons to be meaningful, similar nitric acid concentrations and dissolution conditions must be used.

A plot of percent PuO_2 dissolved in 1 hour versus the initial KF/PuO_2 mole ratio is presented in Figure 7 for the oxides investigated in this work. Parts of the data for PuO_2 (1500°C) were taken from the previous study[1] and are included in this comparison even though the dissolution conditions were slightly different. The difference between the dissolution rates of PuO_2 (1500°C) and the other two oxides would be even more extreme if the former had been dissolved with the "milder" conditions (slightly below the boiling temperature and with no stirring) used for the Mark 40 and Rocky Flats oxides.

The extension of the curves in Figure 7 to the origin has been assumed, but not experimentally confirmed, for the Mark 40 and Rocky Flats PuO_2. This approximation is acceptable for PuO_2

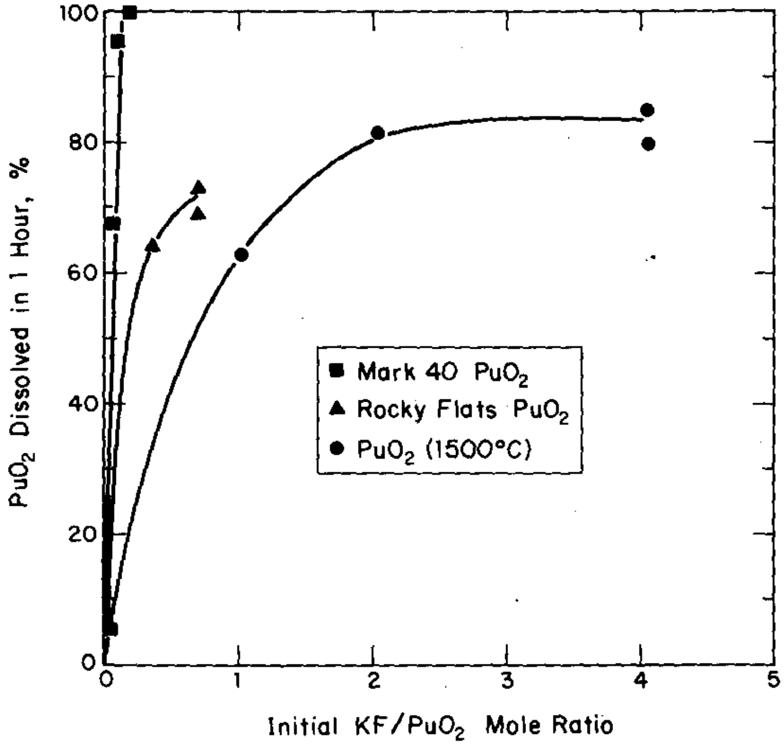

FIGURE 7. Effect of PuO_2 Preparation on Dissolution in $15M\ HNO_3$-KF Solution Solution

(1500°C) because only 0.4 wt % was dissolved after 6 hours in boiling 15M HNO_3 containing no fluoride ion. The data show that for each oxide a different concentration of fluoride ion is required to achieve satisfactory dissolution. The level portion of the curve for PuO_2 (1500°C) suggests that above a certain KF/PuO_2 mole ratio, higher fluoride ion concentrations are not beneficial. As shown by the positions of the curves in Figure 7, the relative dissolubility of the oxide varies: Mark 40 PuO_2 > Rocky Flats PuO_2 > PuO_2 (1500°C). Comparison of this order with information in Table 1 confirms that the KF/PuO_2 mole ratio required for rapid dissolution increases with increasing preparation temperatures.[5] For processing high-fired oxides, such as PuO_2 (1500°C), a lower PuO_2/dissolvent ratio (∿50 g of PuO_2/liter of dissolvent) must be used so that satisfactory dissolution rates can be attained with reasonably low fluoride ion concentrations.

Data for PuO_2 dissolution in HNO_3-Ce(IV) based on the initial Ce(IV)/PuO_2 mole ratio are compared in Figure 8. Included in this comparison are ORNL data for PuO_2 microspheres (Reference 4 and Table 1). The results were converted from instantaneous dissolution rates to percent dissolved in 1 hour using the known

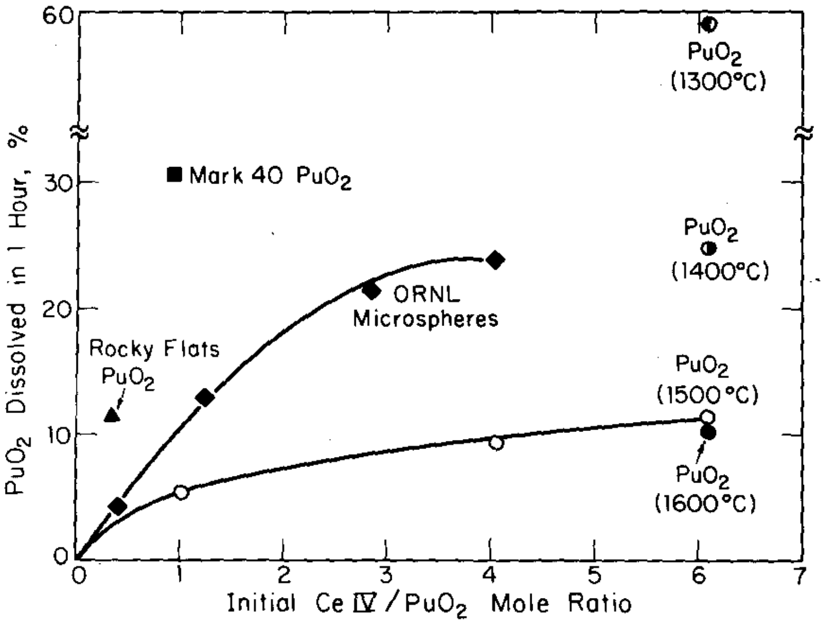

FIGURE 8. Effect of PuO_2 Preparation on Dissolution in 4M HNO_3-Ce(IV) Solution

surface area (assuming it remains constant over the 1-hour period) and the initial weight of PuO_2. Also included in Figure 8 are data for PuO_2 sintered at 1300, 1400, and 1600°C from the previous study.[1] Because data are lacking at several Ce(IV)/PuO_2 mole ratios for each oxide, comparison of dissolution rates is less conclusive than for the HNO_3-F^- system. Based on experiments with Ce(IV)/PuO_2 mole ratios of less than 2, some of the oxides can be tentatively ranked according to their relative dissolubilities as follows: Mark 40 PuO_2 > Rocky Flats PuO_2 > PuO_2 microspheres > PuO_2 (1500°C). A correlation with preparation temperatures is observed as with the HNO_3-F^- data. The effect of sintering temperature was discussed in the previous study.[1] Even after extended dissolving times (up to 24 hours), complete dissolution was not obtained with any of the oxides shown in Figure 8 unless the Ce(IV)/PuO_2 ratio was greater than 2.

REFERENCES

1. H. D. Harmon. *Dissolution of PuO_2 with Cerium(IV) and Fluoride Promoters.* ERDA Report DP-1371, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC (1975).

2. W. E. Unger, et al. *Aqueous Fuel Reprocessing Quarterly Report for Period Ending December 31, 1973.* USAEC Report ORNL-TM-4488, Oak Ridge National Laboratory, Oak Ridge, TN (1974).

3. W. E. Unger, et al. *Aqueous Fuel Reprocessing Quarterly Report for Period Ending March 31, 1973.* USAEC Report ORNL-TM-4240, Oak Ridge National Laboratory, Oak Ridge, TN (1973).

4. W. E. Unger, et al. *Aqueous Fuel Reprocessing Quarterly Report for Period Ending December 31, 1972.* USAEC Report ORNL-TM-4141, Oak Ridge National Laboratory, Oak Ridge, TN (1973).

5. J. D. Moseley and R. O. Wing. *Properties of Plutonium Dioxide.* USAEC Report RFP-503, Dow Chemical Company, Rocky Flats Division, Denver, CO (1965).

6. R. E. Lerch and G. F. Schiefelbein. *The Effect of Fabrication Variables on the Dissolubility of Unirradiated Mechanically Blended Mixed Oxide Fast Reactor Fuel.* USAEC Report WHAN-FR-34, WADCO Corporation, Richland, WA (1970).

7. C. W. Bjorklund and E. Staritzky. *Some Observations on the Reactivity of Plutonium Dioxide.* USAEC Report LA-1869, Los Alamos Scientific Laboratory, Los Alamos, NM (1964).

8. A. L. Uriarte and R. H. Rainey. *Dissolution of High-Density UO_2, PuO_2, and UO_2-PuO_2 Pellets in Inorganic Acids.* USAEC Report ORNL-3695, Oak Ridge National Laboratory, Oak Ridge, TN (1965).

9. G. F. Molen. *Dissolution of Plutonium Oxide.* USAEC Report RFP-922, Dow Chemical Company, Rocky Flats Division, Denver, CO (1967).

10. W. W. Schulz. *Aqueous Decladding and Dissolution of Plutonium Recycle Test Reactor Fuels, Part 2: PuO_2-UO_2 Fuels.* USAEC Report BNWL-204 (Pt. 2), Pacific Northwest Laboratories, Battelle Memorial Institute, Richland, WA (1966).

11. G. S. Barney. *Plutonium Dioxide Dissolution in Nitric/Hydrofluoric Acid Mixtures: Kinetics and Mechanism.* USAEC Report ARH-SA-148, Atlantic Richfield Hanford Company, Richland, WA (1973).

12. D. E. Etter and W. R. Herald. *Plutonium-238 Dioxide Dissolution Study.* USAEC Report MLM-2153, Monsanto Research Corporation, Mound Laboratory, Miamisburg, OH (1974).