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Armen R. Kazanjian
John R. Stevens

Rockwell International

Energy Systems Group
Rocky Flats Plant
P.O. Box 464
Golden, Colorado 80402-0464

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Armen R. Kazanjian and John R. Stevens

ABSTRACT

The dissolution of plutonium dioxide in nitric acid (HNO_3) at high hydrofluoric acid (HF) concentrations has been investigated. Dissolution rate curves were obtained using 12*M* HNO_3 and HF at concentrations varying from 0.05 to 1.0 molar. The dissolution rate increased with HF concentration up to 0.2*M* and then decreased at higher concentrations. There was very little plutonium dissolved at 0.7 and 1.0*M* HF because of the formation of insoluble PuF_4. Various oxidizing agents were added to 12*M* HNO_3-1*M* HF dissolvent to oxidize Pu(IV) to Pu(VI) and prevent the formation of PuF_4. Ceric [Ce(IV)] and silver [Ag(II)] ions were the most effective in dissolving PuO_2. Although these two oxidants greatly increased the dissolution rate, the rates were not as rapid as those obtained with 12*M* HNO_3-0.2*M* HF.

INTRODUCTION

The dissolution of plutonium dioxide plays an important role in the recovery and purification of plutonium. The difficulty in dissolving plutonium dioxide that has been subjected to high temperatures (high-fired oxide) has led to many experimental investigations of the process.[1-5] The most widely used dissolvent is nitric acid-hydrofluoric acid (HNO_3-HF) and most of the investigations have been of this system. Nitric acid is preferred because the resultant nitrate solution is amenable to subsequent processing. However, hydrofluoric acid, which is necessary for acceptably rapid dissolution, is corrosive to equipment and interferes with some of the solvent extraction processes. Investigations have, therefore, been made to develop fluoride-free systems.[6,7] The complexing power of the hydrofluoric acid or fluoride ion (F^-) is very effective, and the dissolution rate obtained with HNO_3-HF appears to be greater than that obtained with any of the fluoride-free systems.

The use of hydrofluoric acid in the Rocky Flats process has not caused major problems and no efforts have been made to eliminate it. The standard dissolvent used at Rocky Flats is 12*M* HNO_3-0.1*M* HF. Since the dissolution rate varies with the HF concentration, increasing the HF concentration to higher values should increase the dissolution rate. Unfortunately, increased dissolution of plutonium dioxide would probably be offset by the precipitation of plutonium tetrafluoride. The calculated solubility of plutonium in 12*M* HNO_3 falls off rapidly in the vicinity of 0.5*M* HF. To take advantage of increased plutonium dioxide dissolution at high HF concentrations, formation of plutonium tetrafluoride must be prevented or the precipitate dissolved. The approach taken in this investigation was to eliminate the precipitate by oxidizing Pu(IV) to Pu(VI).

Oxidizing agents, such as ceric ion, have been used in previous investigations to enhance the dissolution rate.[6] Ozone has also been used experimentally at Rocky Flats to promote the dissolution of plutonium oxide in 12.8*M* HNO_3-0.1*M* HF.[8] The effect on dissolution rate was negligible, probably because of the very small solubility of ozone gas in aqueous solution. However, the results of previous experiments at low fluoride concentrations are not comparable to those obtained in this study. The oxidizing agents added here at HF concentrations of about 1*M* were added primarily to prevent the formation of plutonium tetrafluoride.

Two series of tests were made to determine the dissolution rate of plutonium dioxide in 12*M* HNO_3. In the first series, the HF concentration was varied from 0.05*M* to 1.0*M*. In the second series, several strong oxidizing agents were added to solutions with high HF concentrations to oxidize plutonium to the VI state and prevent the formation of PuF_4. Analyses were made of fluoride concentration, plutonium valence state, and the undissolved residues, as well as the dissolved plutonium, to gain greater understanding of the dissolution process. A few additional experiments were made to examine other factors that would affect dissolution.

EXPERIMENTAL

All the experiments were made using 10-g batches of plutonium dioxide obtained from a single homogenized source. The plutonium dioxide had been calcined at 900 °C for 40 hours and had an assay of 0.878 g/g Pu. Some of the major impurities were 657 ppm Fe, 37 ppm Ni, 120 ppm Ga, 50 ppm C, 143 ppm Al, 21 ppm Ba, 250 ppm Ca, 49 ppm Cr, 36 ppm Mg, and 17 ppm Si. The nitric acid and other reagents were of reagent-grade purity.

The dissolutions were performed in a 250-mℓ Teflon Erlenmeyer flask fitted with a glass condenser. Analysis of the fluoride concentration after boiling a 12*M* HNO_3-0.2*M* HF solution for 6 hours indicated that less than 10 percent of the HF would be lost, either by evaporation or by reaction with glass, during the PuO_2 dissolution experiments. The acid dissolvents were always maintained at 97 °C by immersing the flask in boiling saturated NaCl solution. The same stirring rate was used in all tests.

Eighty milliliters of dissolvent was used for each experiment. The PuO_2 was added to the solution that had been brought to temperature. Two to five milliliters, depending on whether fluoride ion was to be analyzed as well as plutonium, was withdrawn periodically and filtered through a 0.1-micron filter before analysis. Plutonium was analyzed either by X-ray fluorescence (>5 g/ℓ) or radiometrically (<5 g/ℓ). Single determinations were made for each point in the graphs or tables. Fluoride, as both F^- and HF, was analyzed by ion specific electrode after complexing the plutonium in solution. The plutonium valence states were analyzed spectrophotometrically using the 476-nm absorption peak for Pu(IV) analysis and the 831-nm absorption peak for Pu(VI) analysis.[9] The undissolved residues were air dried on the filters and analyzed by X-ray diffraction. The precision of the analysis of PuF_4 by X-ray diffraction was ±5 percent.

RESULTS AND DISCUSSION

The dissolution curves obtained using 12*M* HNO_3 and various concentrations of hydrofluoric acid are shown in Figure 1. The dissolution rate increases with increasing HF concentration up to about 0.2*M* and then starts to decrease. The amount of PuO_2 dissolved in 0.7 and 1.0*M* HF is almost negligible except at the longest period. Dissolution in 0.5*M* HF is an intermediate example in which there is an induction period of about 15 minutes before the PuO_2 starts to dissolve. No explanation can be offered for this induction period. In comparing dissolution rates, the entire curve must be examined. For example, the initial rate is fairly rapid in 0.05*M* HF, but dissolution essentially ceases when the plutonium concentration reaches 20 g/ℓ. Dissolution curves for PuO_2 are always characterized by a continually decreasing rate. The reason for this is that the rate is proportional to the F^- or HF concentration which is reduced by the formation of PuF^{3+} complex as the dissolution proceeds. The fluoride ion concentration is essentially depleted at the highest plutonium concentrations.

To increase the dissolution rate, it is necessary to increase the HF concentration to levels much greater than the plutonium concentration. The plutonium concentration was about 0.3*M* in those experiments with low fluoride concentrations. Unfortunately, PuF_4 is not very soluble and starts to precipitate at HF concentrations of about 0.5*M* as indicated in the last column in Table 1. These calculations were based on a solubility product of 6×10^{-20} for PuF_4.[10] The experimental data in Table 1 show that PuF_4 was precipitated at an HF concentration of 0.3*M*. At HF concentrations of 0.7 and 1.0*M*, there was very little plutonium in solution because of the precipitation of PuF_4. Most of the PuO_2 actually dissolved and was immediately converted to PuF_4.

Various oxidizing agents were used to oxidize Pu(IV) to Pu(VI) and thereby prevent the formation of PuF_4. Table 2 lists the oxidizing agents and their reactions with Pu(IV). Table 3 lists the actual reagents used and their concentrations. One experiment was made with each reagent to determine whether the oxidation rate was rapid enough

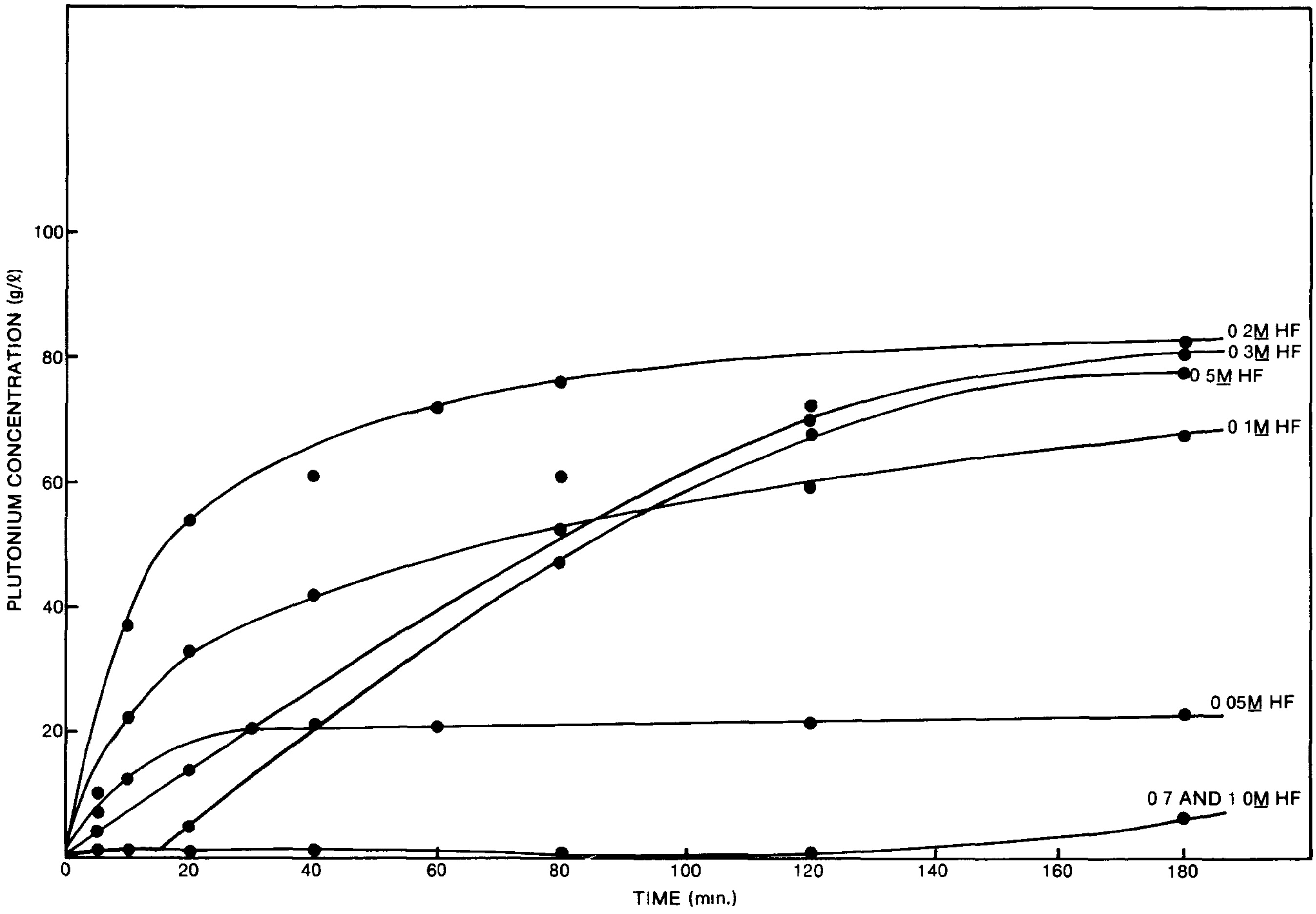

FIGURE 1. Dissolution of PuO_2 in 12*M* HNO_3-HF

TABLE 1. Dissolution of PuO_2 at Various HF Concentrations

HF Concentration (*M*) in 12*M* HNO_3	Undissolved Residue (g)*	Amount PuF_4 in Undissolved Residue		Final HF Concentration (*M*)	Calculated Pu Solubility (g/ℓ)
		Percent	Grams		
0.05	7.3	0	0	0.04	>200**
0.10	4.2	0	0	0.11	>200**
0.30	2.3	69	1.6	0.19	182
0.50	4.3	<50	<2.1	0.12	24
0.70	9.4	78	7.3	0.15	6
1.0	9.0	80	7.0	0.40	1

---

*air-dried weights

**limited by solubility of $Pu(NO_3)_4$

TABLE 2. Oxidation Reactions, Pu(IV) to Pu(VI)

$$2Ce^{4+} + Pu^{4+} + 2H_2O \rightarrow 2Ce^{3+} + PuO_2{}^{2+} + 4H^+$$

$$2MnO_4{}^{1-} + 5Pu^{4+} + 2H_2O \rightarrow 2Mn^{2+} + 5PuO_2{}^{2+} + 4H^+$$

$$Cr_2O_7{}^{2-} + 3Pu^{4+} + 2H^+ \rightarrow 2Cr^{3+} + 3PuO_2{}^{2+} + H_2O$$

$$S_2O_8{}^{2-} + Pu^{4+} + 2H_2O \rightarrow 2SO_4{}^{2-} + PuO_2{}^{2+} + 4H^+$$

$$2Ag^{2+} + Pu^{4+} + 2H_2O \rightarrow 2Ag^{1+} + PuO_2{}^{2+} + 4H^+$$

$$BiO_3{}^{1-} + Pu^{4+} + 2H^+ \rightarrow Bi^{3+} + PuO_2{}^{2+} + H_2O$$

TABLE 3. Dissolution of PuO_2 in 12*M* HNO_3-1.0*M* HF With Added Oxidizing Agents

Oxidizing Agent	Percent Pu(VI) in Solution	Undissolved Residue (g)[a]	Composition of Undissolved Residues
$Ce(NH_4)_2(NO_3)_6$ (0.45*M*)	75	11.0	80% PuF_4 (amorphous or 20% PuO_2 hydrated)
$KMnO_4$ (0.2*M*)	73	11.0	Major compound unidentified, 10% PuO_2
$NaBiO_3$ (0.6*M*)[b]	4	7.6	80% PuF_4 (amorphous) 20% PuO_2
$K_2S_2O_8$ (0.6*M*)	c	9.4	35% PuO_2, remainder unidentified
$K_2Cr_2O_7$ (0.2*M*)[b]	12	6.4	Major compound unidentified, 10% PuO_2
Ag_2O_2 (0.6*M*)[b]	1	26	Major compound $AgNO_3$ about 5% PuO_2
$Ce(NH_4)_2(NO_3)_6$ (0.2*M*)[b] + $K_2Cr_2O_7$ (0.2*M*)	100	2.3	80% PuF_4 (amorphous) 20% PuO_2
$Ce(NH_4)_2(NO_3)_6$ (0.4*M*)[b] + $K_2Cr_2O_7$ (0.4*M*)	75	3.4	70% PuF_3 (crystalline) 30% PuO_2
$K_2S_2O_8$ (0.6*M*) + $AgNO_3$ (0.2*M*)	c	11.4	about 40% PuO_2 remainder unidentified

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a. Air-dried weight.

b. The HF concentration was 0.7*M* rather than 1*M* in these experiments.

c. Pu concentration too low for analysis (<1%).

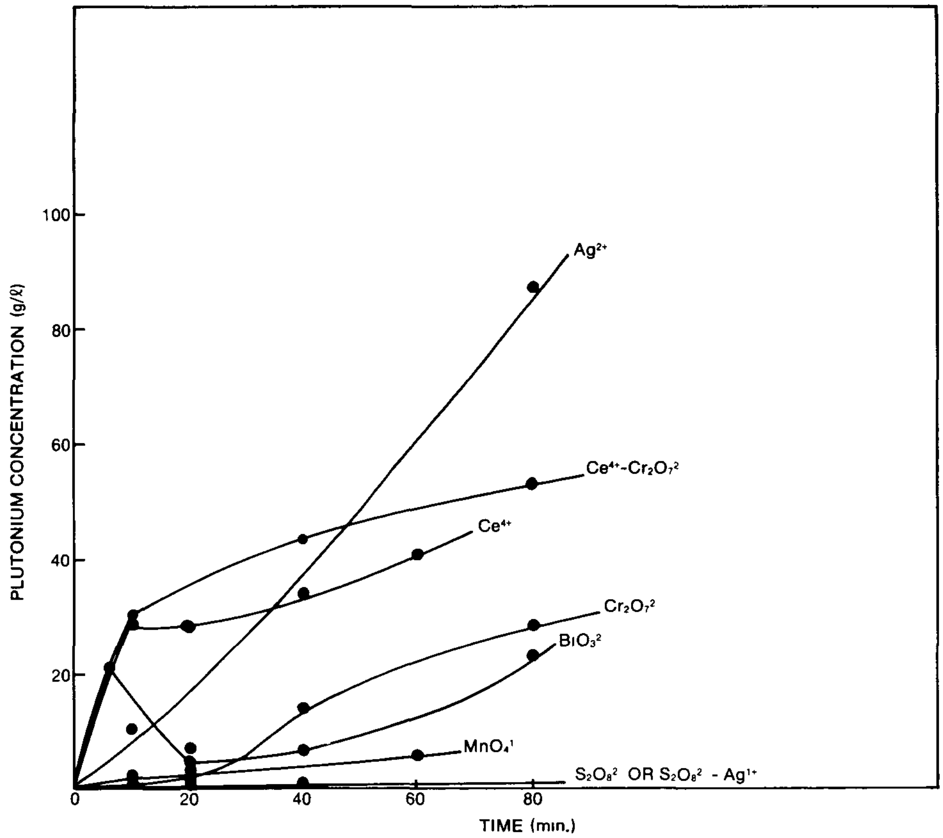
to enhance dissolution. The oxidation potentials of these reagents are adequate to oxidize Pu(IV) to Pu(VI); previous experiments have demonstrated this.[11] The limiting factor is the kinetics of the reaction. Most of these reactions are hindered by high acid concentrations, and unfortunately, the HNO_3 concentration must be maintained at 12*M* for a satisfactory rate of PuO_2 dissolution. Another factor that hinders the oxidation rate is the high fluoride concentration. The complexation and precipitation of plutonium by fluoride ion leaves very little free Pu(IV) available for oxidation.

Nevertheless, some of the oxidizing agents were effective enough to dissolve the plutonium fluoride, as shown in Figure 2. Ceric (Ce^{4+}) and argentic (Ag^{2+}) ions appeared to be superior to the other reagents. The effects of each reagent are discussed individually.

$Ce(NH_4)_2(NO_3)_6$

This reagent has received much attention as a replacement for HF in dissolution with HNO_3.[6] Oxidation of Pu(IV) to Pu(VI) is rapid but optimum acidity for dissolution is 4*M*. Addition of Ce^{4+} in this form also includes the addition of a large amount of unnecessary ammonium nitrate salt. Smaller amounts can be used and electrolytically regenerated as it is reduced, but this procedure was not used in this investigation. The concentration of reagent used (0.45*M*) would oxidize 55 g/ℓ of plutonium stoichiometrically; about 30 g/ℓ was actually achieved. To avoid the excessive amounts of ceric salt necessary to oxidize more plutonium, a combination of ceric and dichromate ions was used as described below. The dissolution results using ceric ion indicate that oxidation occurs rapidly and dissolves a substantial amount of PuF_4.

FIGURE 2. Dissolution With Added Oxidizing Agents



$KMnO_4$

A small amount of plutonium was dissolved in this experiment. Although most of the dissolved plutonium was in the VI valence state, the oxidation rate was apparently not as rapid as the slow decomposition of permanganate ion in hot concentrated acid.

$NaBiO_3$

Although bismuthate ion is a powerful oxidant, the rate of reaction with Pu(IV) appeared to be slow. The initially high dissolution (Figure 2) may be due to analytical error in the first sample. Another experiment was made in which the $NaBiO_3$ was dissolved in acid the day before use. There was very little plutonium dissolved in this case, indicating that bismuthate has a limited stability in concentrated HNO_3 solution. The chemistry of this reagent is not well understood.

$K_2S_2O_8$

Very little plutonium was dissolved, indicating that the oxidation rate was too slow.

$K_2Cr_2O_7$

A significant fraction of the plutonium was dissolved, but the initial rate was very slow.

Ag_2O_2

The initial dissolution rate was not very rapid, but the rate did not decrease with time as it usually does in these dissolution experiments. If the dissolution had been continued for a longer time, all the plutonium would probably have dissolved. The unusual observation in the use of this strong oxidant was that very little of the plutonium was oxidized. No explanation is available for the large dissolution accompanied by the lack of plutonium oxidation. An undesirable side effect of this reagent was the precipitation of a large amount of residue which was analyzed to be silver nitrate.

$Ce(NH_4)_2(NO_3)_6 + K_2Cr_2O_7$

This combination of oxidants has been reported to oxidize Pu(IV) to Pu(VI).[12] The ceric ion apparently acts as a catalyst. Two concentrations of reagents (0.2 and 0.4*M*) were used. Results from the lower concentration were superior and these are the ones plotted in Figure 2. The dissolution curve is similar to that obtained by using cerium alone. The advantage with the combination is that less reagent is required.

$K_2S_2O_8 + AgNO_3$

This combination of reagents was used because the persulfate is strong enough to oxidize Ag^{1+} to Ag^{2+}, and Ag^{2+} may oxidize plutonium faster than persulfate does. The results were not favorable; very little plutonium was dissolved.

ADDITIONAL DISSOLUTION EXPERIMENTS

1. Solubility of PuF_4 as a Function of Temperature

   Dissolutions of PuF_4 were performed at room temperature and 97 °C in 12*M* HNO_3 and in 12*M* HNO_3-1*M* HF. In one set of experiments, 1 g of PuF_4 was stirred in 50 mℓ of 12*M* HNO_3 for 1 hour and filtered. The resulting plutonium in solution was 4.0 g/ℓ at room temperature and 20 g/ℓ at 97 °C, demonstrating an increase in solubility with temperature. In another set of experiments, 1 g of PuF_4 was stirred in 30 mℓ of 12*M* HNO_3-1*M* HF for 6-1/2 hours and filtered. The resulting plutonium in solution was 7.9 g/ℓ at room temperature and 1.0 g/ℓ at 97 °C, demonstrating an inverse temperature effect. Increased solubility at lower temperatures had also been experienced in all the dissolution tests in which a high HF concentration was used. The explanation for this appears to be the increased dissociation of HF (a weak acid) with temperature. More fluoride ion becomes available at higher temperatures to suppress the solubility of PuF_4.

2. Multistage Dissolution

   In one experiment, 10 g of PuO_2 was contacted with four successive 80-mℓ batches of $12M$ HNO_3-$0.1M$ HF. After being stirred for 10 minutes in hot dissolvent, the oxide was filtered and added to a fresh batch of dissolvent. The dissolution rate was faster and displayed a much higher maximum than the rate obtained with a single batch of dissolvent. The results showed that the decrease in rate with time is due to solution content rather than with changes in the solid surface. Calculation of the decrease in surface area of the PuO_2 with time confirms that the decrease in dissolution rate is not due to a decrease in surface area.

3. HF Added in Increments

   Hydrofluoric acid was added periodically to $12M$ HNO_3-$0.2M$ HF during dissolution. The HF concentration was augmented by $0.1M$ at each addition until a final concentration of $0.7M$ was achieved in 1 hour. Dissolution of PuO_2 was continued for another 2 hours. Dissolution proceeded normally until the HF concentration was $0.4M$, did not increase much until the HF reached $0.7M$, and then increased for the next 2 hours, at which time the plutonium concentration was 62 g/ℓ. These results were different from dissolution in $12M$ HNO_3-$0.7M$ HF, in which very little plutonium was dissolved.

4. Preliminary HF Soak

   Ten grams of PuO_2 was allowed to remain in contact with 1.4 mℓ of concentrated HF and 1.4 mℓ of $12M$ HNO_3 for 1 hour. Eighty milliliters of $12M$ HNO_3 was then added and the mixture heated and stirred for 2 hours. The fluoride concentration in the 80 mℓ dissolvent was $0.5M$. The resultant dissolution curve did not exhibit the induction period that is obtained with dissolution in $12M$ HNO_3-$0.5M$ HF (Figure 1). Nevertheless, the dissolution rate at the beginning of the run was not very rapid. Another experiment in which $1M$ $NaNO_2$ was added to $12M$ HNO_3-$0.5M$ HF to eliminate the induction period was unsuccessful.

CONCLUSIONS

The experiments demonstrated that oxidation of plutonium to the Pu(VI) state prevents the precipitation of PuF_4 and greatly improves the dissolution rate of PuO_2 in solutions with high HF concentrations. However, the oxidation rates are not adequate to produce an overall dissolution rate that is faster than that obtained with $12M$ HNO_3-$0.2M$ HF. An oxidant or combination of oxidants that would oxidize Pu(IV) more rapidly is required.

Other experiments showed that the solubility of PuF_4 was reduced at elevated temperatures and that the decrease in dissolution rate of PuO_2 with time is due to solution content rather than decrease in surface area.

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