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DISSOLUTION OF PuO_2 WITH CERIUM(IV) AND FLUORIDE PROMOTERS

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

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by

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ABSTRACT

Ce(IV), fluoride, and Ce(IV)-fluoride mixtures were investigated as promoters for nitric acid dissolution of refractory PuO_2.

Ce(IV) in low concentrations is an effective promoter of PuO_2 dissolution in nitric acid solutions of approximately 3 to 6M. However, stoichiometric quantities of Ce(IV) are required for complete dissolution, and hydrothermal precipitation of CeO_2 is a potential problem at low acidities. Dissolution proceeds with oxidation of Pu(IV) to Pu(VI) with a corresponding reduction of Ce(IV). When an excess of Ce(IV) is present, the dissolution rate depends on Ce(IV) concentration below ∿0.1M Ce(IV); above this concentration, the rate becomes fairly constant. Increased PuO_2 sintering temperature markedly reduces the dissolution rate in 4M HNO_3-0.15M Ce(IV). Preliminary results indicate stainless steel corrosion rates in Ce(IV)-HNO_3 solutions increase to significant values with increasing Ce(IV) concentration.

In HNO_3-KF, the PuO_2 dissolution rate increases rapidly as the nitric acid and fluoride concentrations increase. The rate is decreased by increased PuO_2 sintering temperature and the presence of cationic species such as UO_2^{2+} and Fe^{3+}, which complex fluoride. Dissolution is much more rapid in HNO_3-KF solutions than in HNO_3-Ce(IV).

Mixed KF and Ce(IV) in certain mole ratios in 8M HNO_3 gives more rapid dissolution than with Ce(IV) or KF alone; more Ce(IV) retards dissolution. In HNO_3-0.05M Ce(IV)-0.1M KF, the dissolution rate increases as HNO_3 concentration increases; below 6M HNO_3, the mixed system containing 0.05M Ce(IV)-0.1M KF is less effective than HNO_3-Ce(IV) or HNO_3-KF.

Ruthenium, present in irradiated PuO_2, catalytically reduces Ce(IV) in nitric acid; thus, Ce(IV) will be ineffective for irradiated PuO_2-UO_2 fuel. In view of the ruthenium problem, HNO_3-F^- solutions appear most promising for breeder fuel processing. Nitric acid solutions containing Ce(IV) and Ce(IV)-F^- mixtures may be most useful for dissolving unirradiated PuO_2 and UO_2-PuO_2 materials, as in scrap recovery operations.

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DISSOLUTION OF PuO_2 WITH CERIUM (IV) AND FLUORIDE PROMOTERS

INTRODUCTION

It is well known that the dissolution rate of PuO_2 in HNO_3 solutions is greatly increased by the addition of fluoride.[1,2,3] HNO_3-fluoride solutions are currently regarded as the most suitable dissolvents for reprocessing of UO_2-PuO_2 breeder fuels such as those from the Fast Flux Test Facility (FFTF) and from the liquid metal fast breeder reactors (LMFBR). However, since HNO_3-fluoride solutions are extremely corrosive to stainless steel equipment, alternative dissolution promoters for these fuels are being sought.

The beneficial effect of Ce(IV) on the dissolution rate of PuO_2 powder in nitric acid was first reported in 1942[4] and later was patented by A. S. Wilson.[5] Uriarte and Rainey[1] studied the instantaneous dissolution rate (IDR) of PuO_2 pellets in the HNO_3-Ce(IV) system and concluded that the rate increase was too small for practical application. However, recent studies at Oak Ridge National Laboratory (ORNL) showed that Ce(IV) substantially enhances the dissolution of PuO_2 microspheres and UO_2-PuO_2 pellets.[6-10]

In view of these results, laboratory studies were undertaken to investigate the effect of Ce(IV) in promoting the dissolution of PuO_2 by nitric acid and nitric acid-hydrofluoric acid mixtures.

EXPERIMENTAL

Dissolution Procedure

Dissolution experiments were conducted in 125-ml Erlenmeyer flasks equipped with a condenser and modified to facilitate sampling. Weighed quantities of PuO_2 ($\sim$0.5 g) were mechanically stirred in 75 ml of dissolvent at the desired temperature (normally boiling). Samples were withdrawn periodically, and the percent dissolution was calculated from the initial weight of PuO_2 and the gross alpha analyses of the solution.

Analyses

Plutonium was determined by gross alpha and alpha pulse height analyses of 100-microliter aliquots evaporated on stainless steel planchets. Ce(IV) analyses were made by standard ferrous sulfate titration in 0.5M H_2SO_4 to the ferroin end point. Acid was determined by pH titration with KF added to complex hydrolyzable cations. Free fluoride ion measurements were conducted with a specific fluoride ion electrode (Orion Model 94-09)* and the appropriate calibration curve. Total fluoride was measured by a similar method[11] using phosphoric acid to complex cations and free the fluoride for detection. Electromotive force was measured using a combination platinum redox electrode (Orion Model 96-78).* Precipitates were characterized by spark-source mass spectrometry and x-ray diffraction techniques.

Chemicals

PuO_2 was prepared from plutonium metal by dissolution in 8M HNO_3-0.05M KF followed by precipitation of plutonium(III) oxalate and calcination for 2 hours at 700°C.[12] Portions of the resulting oxide were sintered at 1300, 1400, 1500, and 1600°C for 4 hours in 4% H_2-He atmosphere.

Stock solutions were prepared from reagent-grade nitric acid, ceric ammonium nitrate, and potassium fluoride dihydrate.

PuO_2 DISSOLUTION IN HNO_3-Ce(IV) SOLUTIONS

Effect of HNO_3 Concentration

The effect of HNO_3 concentration on PuO_2 dissolution was investigated in experiments with a constant Ce(IV) concentration of 0.05M and varying HNO_3 concentrations of 0.5 to 15M. The results in Figure 1 are in agreement with ORNL results with PuO_2 microspheres;[6] the maximum dissolution is observed at 4M HNO_3. The decreased dissolution above and below 4M HNO_3 was not anticipated; possible explanations for this behavior are presented in later sections. These results indicate that the HNO_3 concentration range of 3-6M will be most effective and will dissolve approximately 37-41% in 6 hours with 0.05M Ce(IV).

Effect of Ce(IV) Concentration

Experiments were conducted to determine the optimum Ce(IV) concentration for PuO_2 dissolution in 4M HNO_3. The percent dissolution depends on the Ce(IV) concentration below ∿0.1M Ce(IV), as shown in Figure 2. Above this concentration the dissolution rate is fairly constant. This cannot be explained by a deficiency of Ce(IV), because after the 6-hour dissolving period, an excess of

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* Orion Research Incorporated, Cambridge, Mass.

Ce(IV) was still present in all cases. The change in behavior above ∿0.1M Ce(IV) may be due to a change in the Ce(IV) species in solution or an unfavorable Ce(IV)/Ce(III) ratio.

Additional dissolutions with 4.0M HNO_3-0.025M Ce(IV) and 4.0M HNO_3-0.15M Ce(IV) for extended times were conducted to determine the maximum attainable dissolution. These results are shown in Figure 3. With 0.025M Ce(IV), the dissolution rate leveled off after ∿13 hours, and a considerable portion of the PuO_2 remained undissolved. This may be explained by depletion of Ce(IV) because the 0.15M Ce(IV) solution, which gave complete dissolution, contained a considerable excess above that needed to oxidize all the Pu(IV).

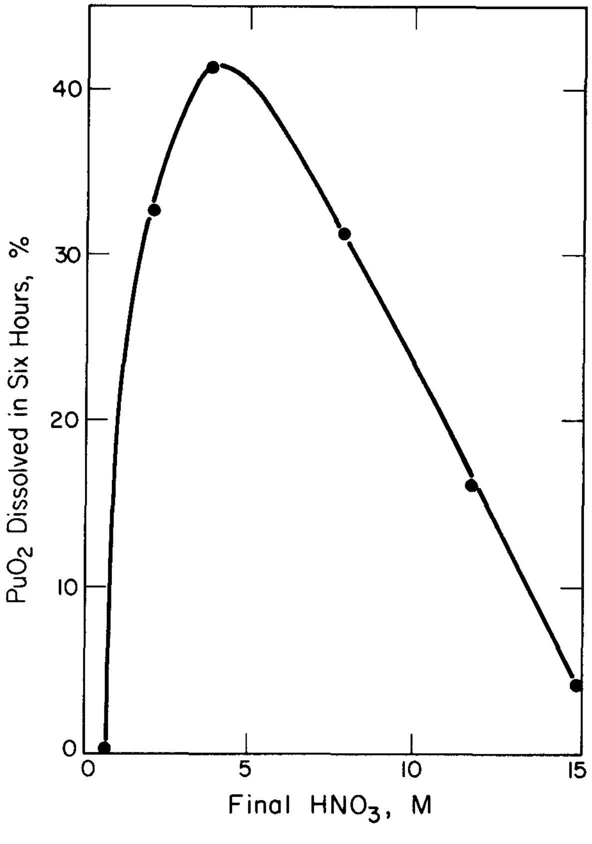

FIG. 1 EFFECT OF HNO_3 ON THE DISSOLUTION OF PuO_2 IN 0.05M Ce(IV) (6 hours at boiling temperature)

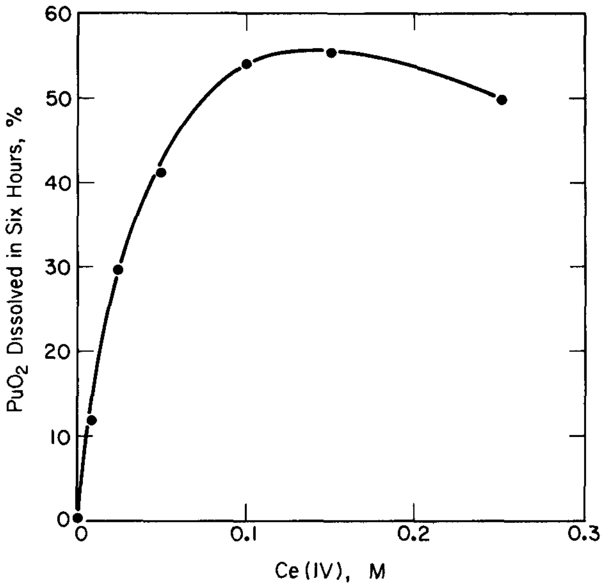

FIG. 2 EFFECT OF Ce(IV) ON THE DISSOLUTION OF PuO_2 IN 4M HNO_3 (6 hours at boiling temperature)

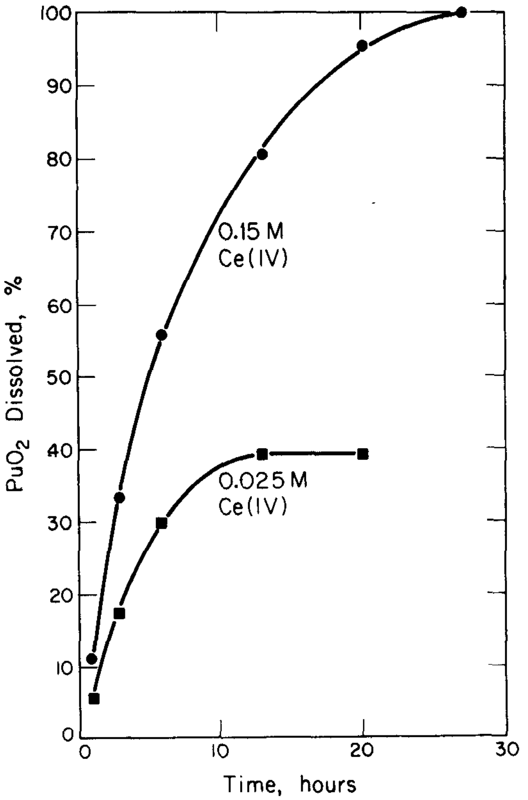

FIG. 3 EFFECT OF TIME ON THE DISSOLUTION OF PuO_2 in 4M HNO_3 - Ce(IV)

Therefore, the role of Ce(IV) in the dissolution process is not as a true catalyst since it is required in stoichiometric amounts. Thus, to dissolve PuO_2 to high concentration solutions would require large Ce(IV) concentrations, i.e., ∿0.4M Ce(IV) would be required to produce ∿44 g Pu/ℓ. Such a concentration of Ce(IV) may present serious corrosion problems because preliminary studies have shown that corrosion of 304L stainless steel increases with Ce(IV) concentration (see Table 1).

TABLE 1

Corrosion of 304L Stainless Steel in Boiling Nitric Acid - Ceric Ammonium Nitrate Solutions

Exposure Time, days	Corrosion Rate, mils/yr 4M HNO_3-0.05M CAN[a]	8M HNO_3-0.05M CAN[a]
7	17.4	27.4
11	--	19.6
14	37.4	--
35	--	11.8
37	85.8	--

Exposure Time, days	Corrosion Rate, mils/yr 12M HNO_3-0.05M CAN[a]	12M HNO_3-0.10M CAN[a]
7	49.1	113
11	46.2	102
35	65.9	110

---

[a] CAN = ceric ammonium nitrate.

Effect of Ce(III) on PuO_2 Dissolution

Wilson[5] reported that in boiling 16M HNO_3, Ce(III) was as effective as Ce(IV) in promoting PuO_2 dissolution. ORNL results showed that the Ce(III) effect is quite small (if it exists at all) unless the HNO_3 concentration is greater than 12M.[6,7,8] These reports indicate that the PuO_2 dissolving effect of Ce(III) simply results from oxidation of a portion of the Ce(III) to Ce(IV), which promotes dissolution.

Measurements of Ce(III) oxidation by boiling HNO_3 solutions are summarized in Figure 4. These data confirm that Ce(III) is oxidized to Ce(IV) in the nitric acid systems used for PuO_2 dissolution.

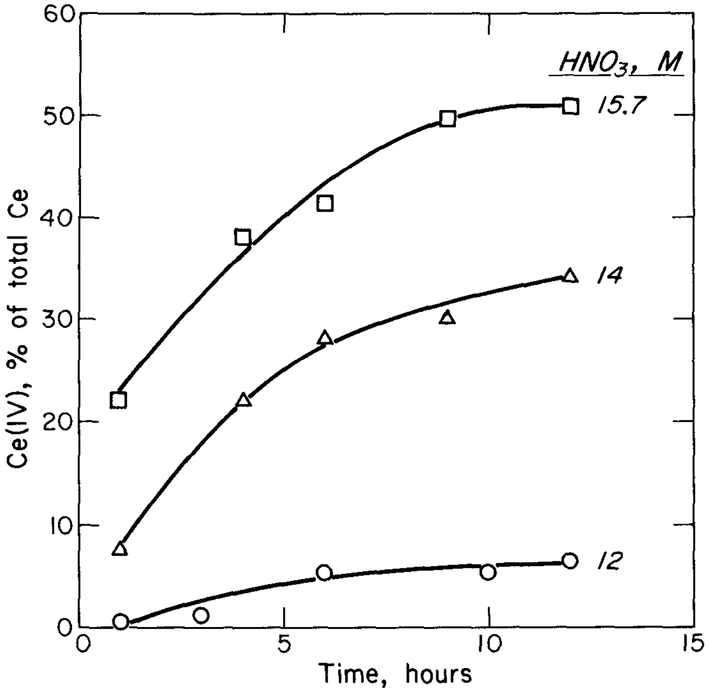

FIG. 4 OXIDATION OF Ce(III) BY BOILING HNO_3

Hydrothermal Precipitation of CeO_2

During PuO_2 dissolution with 0.5M HNO_3-0.05M Ce(IV), a white precipitate formed as the solution was heated to near the boiling point. Precipitation was also reported by ORNL workers with 1M HNO_3-0.1M Ce(IV).[6] The white solid in our work was identified as CeO_2. Ceric ammonium nitrate solutions have been observed to precipitate CeO_2 under pressure at elevated temperatures.[13,14] This phenomenon, called hydrothermal precipitation, has been observed for several other salts including $AlCl_3$, $Al(NO_3)_3$, $ThCl_4$, $Th(NO_3)_4$, $Fe(NO_3)_3$, and $UO_2(NO_3)_2$.[14,15,16]

The hydrothermal precipitation of CeO_2 was studied[17] to determine the limitations, if any, that this phenomenon may impose on PuO_2 dissolution in HNO_3-Ce(IV) solutions. It was concluded that precipitation of CeO_2 should not occur to a significant extent if the HNO_3 concentration is maintained at >2M

(Figure 5). Solutions will be stable at lower acid concentrations than 2M when significant salt concentrations are present. However, when the solution is diluted to <1M HNO_3, the temperature should not exceed 60°C for prolonged periods to avoid any possibility of CeO_2 precipitation.

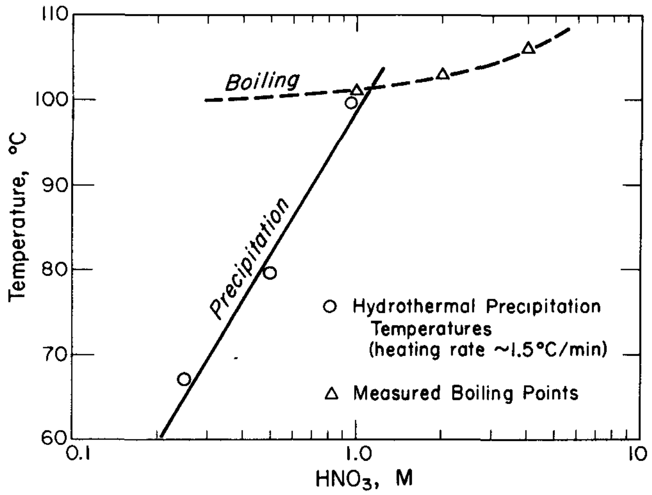

FIG. 5 HYDROTHERMAL PRECIPITATION OF CeO_2 FROM HNO_3 - 0.05M Ce(IV) SOLUTIONS

Effect of Dissolvent Temperature

As discussed above, 0.5M HNO_3-Ce(IV) solutions are unstable above 78°C at heating rates of approximately 1.5°C/min.[17] At 60°C, however, dilute HNO_3-0.025M Ce(IV) solutions are sufficiently stable over extended time periods for use in PuO_2 dissolution. Table 2 shows slightly increased PuO_2 dissolution at 60°C for 0.5M HNO_3. Presumably this is due to avoiding loss of Ce(IV) by hydrothermal precipitation. In agreement with ORNL results,[7] the dissolution rate in 4M HNO_3-Ce(IV) is significantly reduced by lowering the temperature.

TABLE 2

Effect of Temperature on
PuO_2 Dissolution by HNO_3-0.025M Ce(IV) Solutions

	% Dissolved in Six Hours	
HNO_3, M	60°C	Boiling
0.5	0.49	0.16
1.0	5.4	5.3
4.0	2.7	29.6

Effect of PuO_2 Sintering Temperature

Since the thermal history of PuO_2 has a significant effect on its dissolution properties,[18] the effect of PuO_2 sintering temperature on dissolution in 4M HNO_3-0.15M Ce(IV) was investigated. The results in Figure 6 show that PuO_2 is more difficult to dissolve as the sintering temperature increases. The opposite effect has been reported for mixed PuO_2-UO_2;[18] high sintering temperature apparently improves dissolubility of the mixed oxide by promoting solid solution formation.

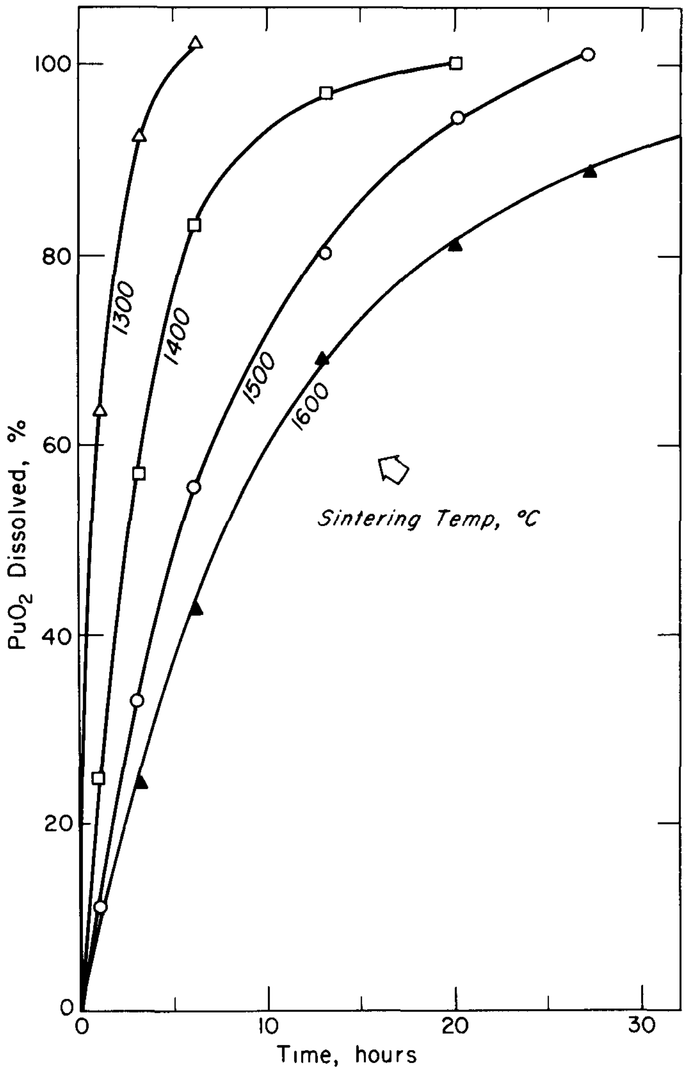

FIG. 6 EFFECT OF SINTERING TEMPERATURE ON PuO_2 DISSOLUTION IN 4M HNO_3 - 0.15M Ce(IV)

Effect of Complexing Anions

The effect of the complexing anions SO_4^{2-} and F^- on PuO_2 dissolution rate in 8M HNO_3-0.05M Ce(IV) is shown in Table 3. Dissolution is definitely enhanced by the presence of these anions, with a more substantial effect indicated for the Ce(IV)-F^- system. Ce(IV) may serve the dual purpose in the latter system of promoting PuO_2 dissolution and complexing F^- for corrosion protection. Detailed studies of this system are discussed in succeeding sections.

TABLE 3

Effect of Fluoride and Sulfate on the Dissolution of PuO_2 in 8M HNO_3-0.05M Ce(IV)

Solution	% Dissolved	
	3 hr	6 hr
8M HNO_3-0.05M Ce(IV)	21.5	31.4[a]
8M HNO_3-0.05M Ce(IV)-0.1M H_2SO_4	28.2	35.5
8M HNO_3-0.05M Ce(IV)-0.1M KF	38.9[a]	76.9[a]

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a. Average of duplicate measurements.

The Dissolution Reaction Mechanism

The results discussed above provide information concerning the reaction mechanism for dissolving PuO_2 in HNO_3-Ce(IV) solutions. ORNL workers have shown that the dissolution proceeds with oxidation of all the Pu(IV) to Pu(VI) with a corresponding reduction of Ce(IV).[8]

(1) $2Ce(IV) + Pu(IV) \rightarrow Pu(VI) + 2Ce(III)$

Potentiometric measurements have indicated that $Ce(OH)^{3+}$ is the principal Ce(IV) species in 0.5-2.0M perchloric acid.[19] The present data indicate that $Ce(OH)^{3+}$ or some other active species predominates near 4M HNO_3. At higher HNO_3 concentrations, hydrolysis is certainly reduced, and the tendency to form $Ce(OH)^{3+}$ is replaced by the formation of cerium nitrate complexes that evidently are less active oxidizing species. Seaborg and Katz[20] have stated that the oxidation of Pu(IV) to Pu(VI) by Ce(IV) is slowed by the presence of ions that are capable of complexing both Pu(IV) and Ce(IV). Also, Krause[21] has shown that both increasing acidity and increasing nitrate concentration retard the rate of oxidation of Pu(IV) to Pu(VI) in HNO_3.

The decrease in PuO_2 dissolution rate below 4M HNO_3 may be related to the hydrothermal precipitation of CeO_2. Under favorable conditions, it seems likely that the following reaction can occur and thereby remove the active Ce species from solution:

$$Ce(OH)^{3+} + H_2O \rightarrow CeO_2 + 3H^+ \tag{2}$$

Additional hydrolysis of Ce(IV) to form $Ce(OH)_2{}^{2+}$ has been reported.[19] It is also possible that CeO_2 could be formed from this species as shown in Reaction 3:

$$Ce(OH)_2{}^{2+} \rightarrow CeO_2 + 2H^+ \tag{3}$$

The leveling of the dissolution rate in 4M HNO_3 at higher Ce(IV) concentrations may also be related to removal of the active Ce(IV) species. Evidence for polymeric cerium species has been observed,[22] and polymerization would certainly be expected to be more advanced at the higher Ce(IV) concentrations. The binding of the metal ions in such polymeric species is believed to be by oxide or hydroxide bridging.[22] Therefore, an active species such as $Ce(OH)^{3+}$ could possibly become polymerized to an inactive state when the Ce(IV) concentration is increased sufficiently.

PuO_2 DISSOLUTION IN HNO_3-KF SOLUTIONS

Effect of HNO_3 and Fluoride Concentrations

The effect of nitric acid and fluoride ion concentrations on PuO_2 dissolution was determined and compared with HNO_3-Ce(IV) dissolution. As shown in Figure 7, the dissolution rate increases rapidly as the nitric acid and fluoride concentrations increase; similar effects have been reported by other workers.[1,2]

The apparent reversal of dissolution rate after 2 hours for 12 and 15M HNO_3 is probably due to experimental uncertainty; the magnitude of this uncertainty is shown by the variation between duplicate runs for 8M and 15M HNO_3.

Effect of PuO_2 Sintering Temperature

The effect of sintering temperature on PuO_2 dissolution in 7M HNO_3-0.6M $UO_2(NO_3)_2$-0.23M $Fe(NO_3)_3$-0.1M KF was measured. This solution composition is representative of the latter stages of dissolution of PuO_2-UO_2 fuel. The results in Figure 8 show the anticipated trend of decreased dissolution rates as sintering temperature increases.

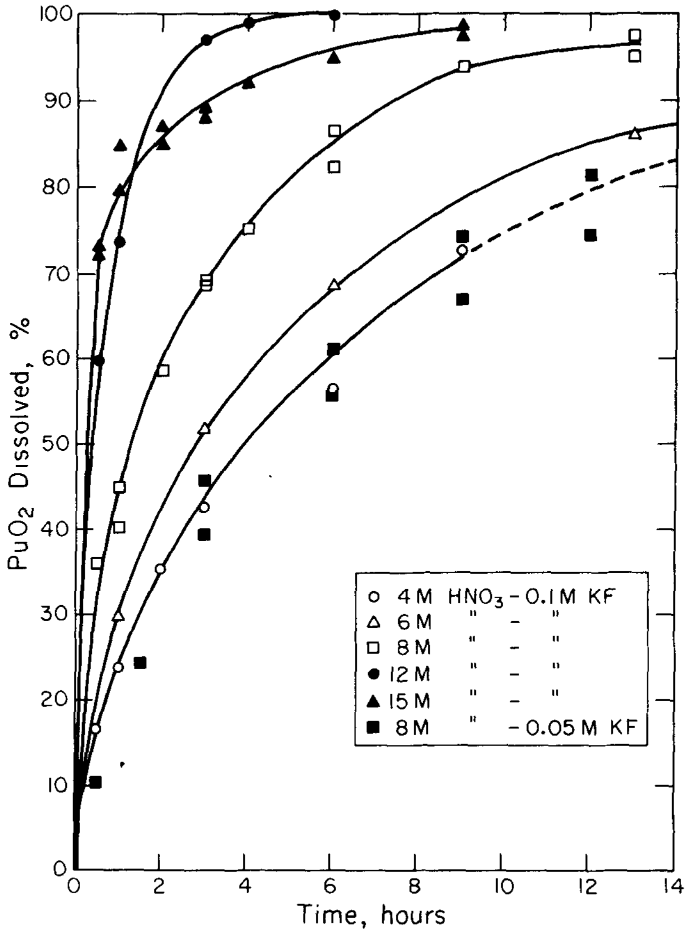

FIG. 7 EFFECT OF HNO_3 AND FLUORIDE CONCENTRATIONS ON PuO_2 DISSOLUTION

Effect of the Presence of UO_2^{2+} and Fe^{3+} in the Dissolvent

Dissolution of PuO_2 sintered at 1500°C in 6M HNO_3-0.1M KF was much more rapid than that in 7M HNO_3-0.6M $UO_2(NO_3)_2$-0.23M $Fe(NO_3)_3$-0.1M KF even though the acid concentration was lower (Figure 8). This effect is largely due to complexing of fluoride by UO_2^{2+} and Fe^{3+}. Therefore, the time required for dissolving mixed PuO_2-UO_2 fuel will be long unless the initial dissolver solution is removed, and fresh HNO_3-KF is added to complete the PuO_2 dissolution. As shown in Table 4, the presence of UO_2^{2+} and Fe^{3+} in the dissolvent decreases stainless steel corrosion rates in 9M HNO_3-0.1M KF. Thus, the relative advantages of retarded dissolver corrosion versus faster fuel dissolution must be balanced.

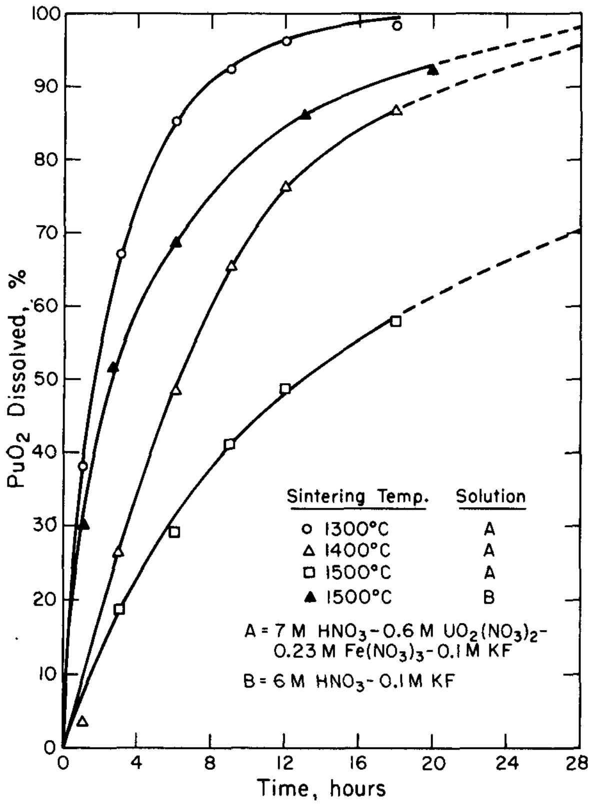

FIG. 8 EFFECT OF SINTERING TEMPERATURE ON PuO_2 DISSOLUTION

TABLE 4

Corrosion of 304L Stainless Steel in Boiling 9M HNO_3-0.1M KF Solutions

Exposure Time, hours	Corrosion Rate, mils/yr 9M HNO_3-0.1M KF	9M HNO_3-0.1M KF-0.6M $UO_2(NO_3)_2$
3	502	843
8	1074	1274
13	2234	1845

Exposure Time, hours	Corrosion Rate, mils/yr 9M HNO_3-0.1M KF-0.23M $Fe(NO_3)_3$	9M HNO_3-0.1M KF-0.23M $Fe(NO_3)_3$-0.6M $UO_2(NO_3)_2$
3	277	49
8	431	67
13	906	146

PuO_2 DISSOLUTION IN HNO_3-Ce(IV)-KF SOLUTIONS

The enhancement of PuO_2 dissolution by SO_4^{2-} and F^- in 8M HNO_3-0.05M Ce(IV) was discussed previously. The more significant effect of F^- was studied further.

Effect of HNO_3 Concentration

The effect of varying the HNO_3 concentration with 0.05M Ce(IV) and 0.1M KF was studied. As in the HNO_3-KF system, the dissolution rate steadily increased as the HNO_3 concentration was increased (Figure 9).

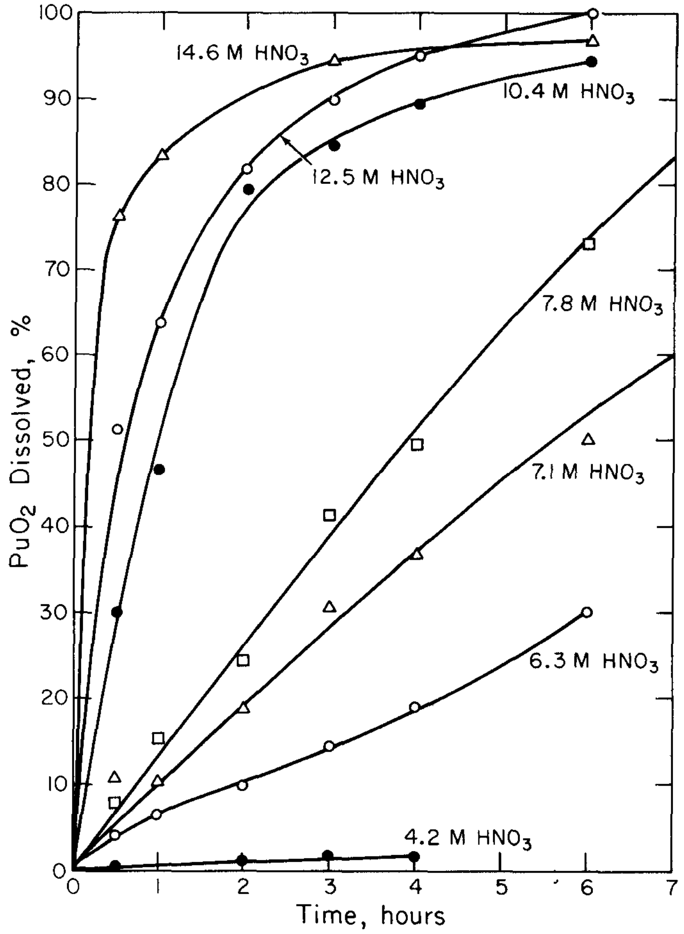

FIG. 9 EFFECT OF HNO_3 CONCENTRATION ON PuO_2 DISSOLUTION IN HNO_3 - 0.05M Ce(IV) - 0.1M KF

Effect of Ce(IV) Concentration

The optimum Ce(IV) concentration for PuO_2 dissolution in 8M HNO_3 containing 0.05 and 0.1M KF was determined. Data for 8M HNO_3-0.05M KF solutions are shown in Figure 10. The optimum KF/Ce(IV) ratio for 8M HNO_3-0.05M KF and 8M HNO_3-0.1M KF is illustrated in Figure 11. Maximum dissolution rates are indicated at 0.025M Ce(IV) for both 0.05M KF [2KF/Ce(IV)] and 0.1M KF [4KF/Ce(IV)]. At higher Ce(IV) concentrations, the dissolution rate decreases presumably due to increased complexing of F^- by Ce(IV). Since Pu(IV) also strongly complexes F^-, the optimum KF/Ce(IV) ratio may vary with the quantity of PuO_2.

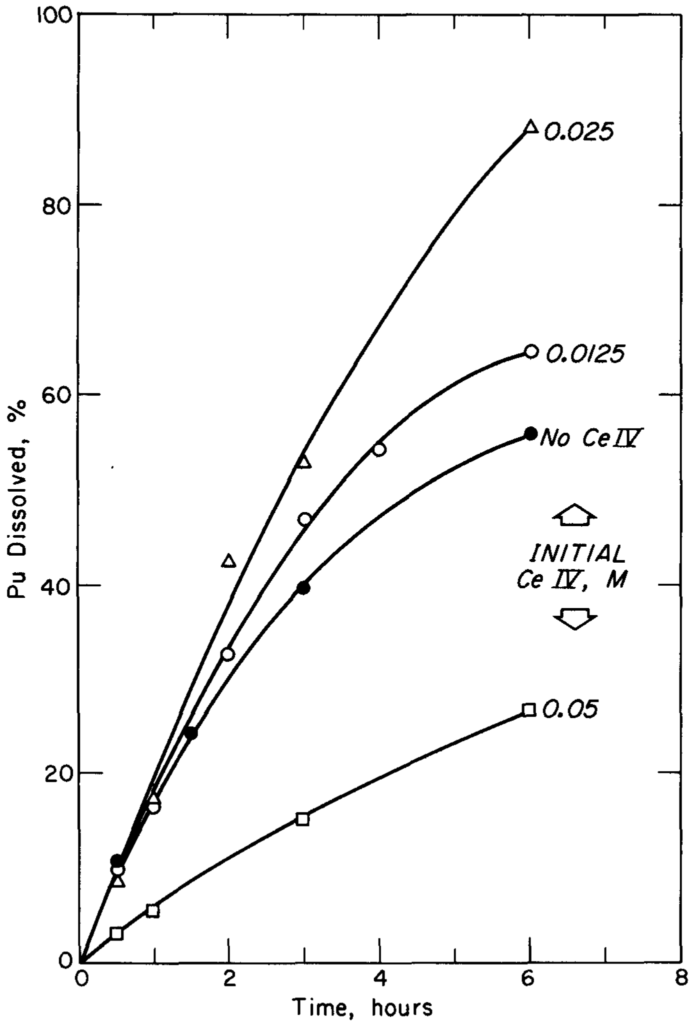

FIG. 10 EFFECT OF Ce(IV) ON DISSOLUTION OF PuO_2 IN 8M HNO_3 - 0.05M KF

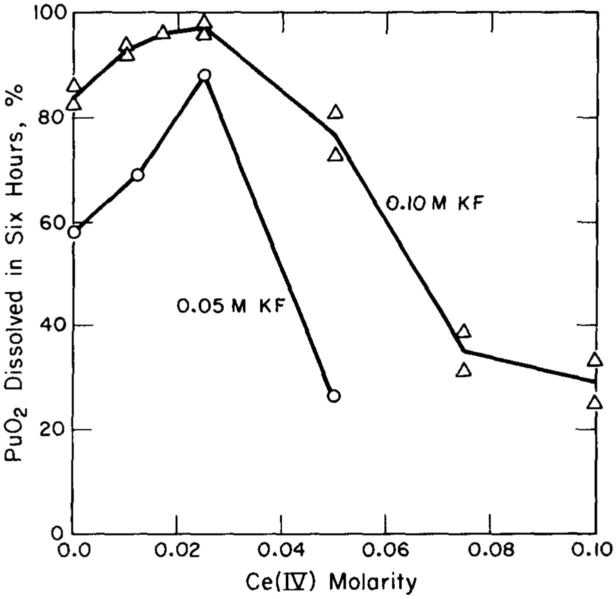

FIG. 11 EFFECT OF Ce(IV) CONCENTRATION ON PuO_2 DISSOLUTION IN 8M HNO_3 - KF

Effect of Fluoride Concentration

The effect of increasing fluoride concentration on PuO_2 dissolution in 8M HNO_3-0.05M Ce(IV) is illustrated in Figure 12. Addition of 0.05M KF slightly lowers the dissolution rate initially, but increases the total quantity of PuO_2 dissolved. This can occur because dissolution with Ce(IV) alone is limited by the total Ce(IV) concentration; when all the Ce(IV) is reduced to Ce(III), dissolution almost stops (see Figure 5). With fluoride present, the dissolution reaction proceeds to completion. Since a KF/Ce(IV) ratio of 1.0 is not optimum, increasing the fluoride concentration above 0.05M KF approaches a more favorable ratio and causes a rapid increase in dissolution rate.

Beneficial Effect of Mixed Ce(IV) and KF

The dissolution studies discussed above have confirmed that there is a definite beneficial effect from mixed Ce(IV) and KF at certain KF/Ce(IV) ratios. The data in Table 5 (see Figure 17 also) indicate that, after 3-6 hours, the amount of PuO_2 dissolved by the optimum mixed system is nearly equal to the sum of the amounts dissolved by each promoter alone. At other KF/Ce(IV) ratios, the amount dissolved is not fully additive (see Figure 11); in fact, at a KF/Ce(IV) ratio of 1.0, the mixed system dissolves less than either promoter alone.

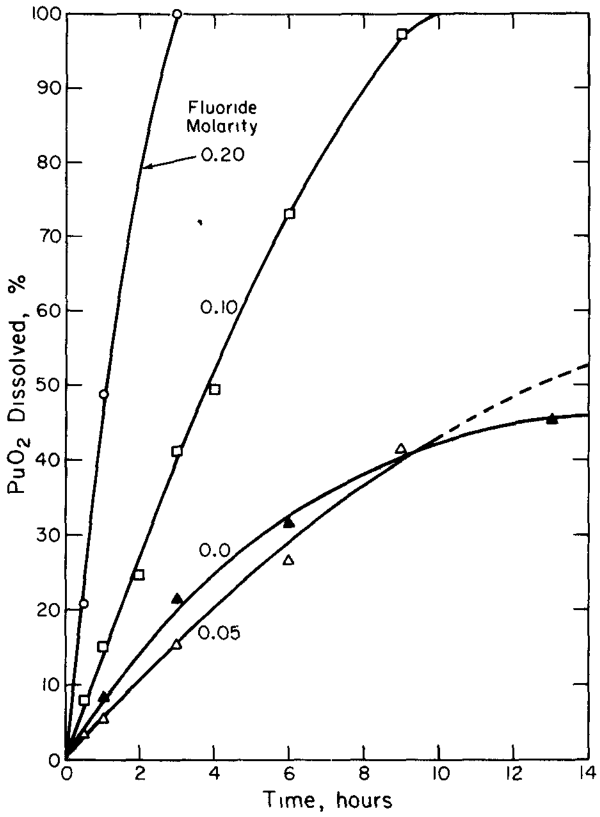

FIG. 12 EFFECT OF FLUORIDE CONCENTRATION ON PuO_2 DISSOLUTION IN $8M\ HNO_3$ - 0.05M Ce(IV)

TABLE 5

Effect on PuO_2 Dissolution of Mixing Ce(IV) and KF in $8M\ HNO_3$

Dissolving Time, hours	PuO_2 Dissolved, %			
	0.025M Ce(IV)	0.05M KF[a]	Sum[b]	0.025M Ce(IV)-0.05M KF
1	6.3	34.7	41.0	17.4
3	19.0	42.6	61.6	52.8
6	31.2	58.5	89.7	88.2
	0.025M Ce(IV)	0.1M KF[a]	Sum[b]	0.025M Ce(IV)-0.1M KF[a]
1	6.3	42.6	48.9	29.0
3	19.0	68.8	87.8	86.3
6	31.2	84.4	>100	97.0

---

[a] Average of duplicate experiments.

[b] Sum of the amount dissolved by each promoter when used separately.

Decomposition of 8M HNO_3-Ce(IV)-0.1M KF Solutions

A series of 8M HNO_3-Ce(IV)-0.1M KF solutions that had been stored in polyethylene containers for 3-6 months were analyzed for Ce(IV) content. Table 6 indicates significant decomposition. Inspection of the storage containers revealed the presence of a white solid (not identified) in the more dilute Ce(IV) solutions, in which decomposition was most rapid. Since freshly prepared solutions were used in all dissolution studies, no attempt has been made to relate solution stability and effectiveness as a PuO_2 dissolvent. These results primarily confirm the need for using freshly prepared HNO_3-Ce(IV)-KF solutions.

TABLE 6

Decomposition of 8M HNO_3-Ce(IV)-0.1M KF Solutions

Initial Ce(IV), M	Final Ce(IV), M	Days in Storage	% Decomposed	Average Decomposition Rate, %/day
0.10	0.053	118	47	0.40
0.075	0.061	85	19	0.22
0.050	0.035	152	29	0.19
0.025	0.0078	120	69	0.57
0.017	0.0024	119	86	0.72
0.010	0.00093	111	91	0.82

Effect of Fluoride on emf of 8M HNO_3-Ce(IV) Solutions

To gain more understanding of the 8M HNO_3-Ce(IV)-KF systems used in the dissolution studies, the effect of fluoride ion on the emf of these solutions was determined. Studies at ORNL[8,9,10] have shown that the emf of an HNO_3-Ce(IV) solution may be used as an indicator of the solution's effectiveness as a PuO_2 dissolvent. Their results indicated that an emf of about 1.4 V is needed for reasonably rapid dissolution of PuO_2 microspheres.

In Figure 13, the emf measurements for a series of 8M HNO_3-Ce(IV)-0.1M KF solutions without plutonium present are compared to values for solutions of 8M HNO_3-Ce(IV) containing no fluoride. As expected, the presence of 0.1M KF lowers the emf of these solutions presumably by cerium(IV)-fluoro complex formation. The emf is maintained above 1.4 V until the Ce(IV) concentration is <0.01M.

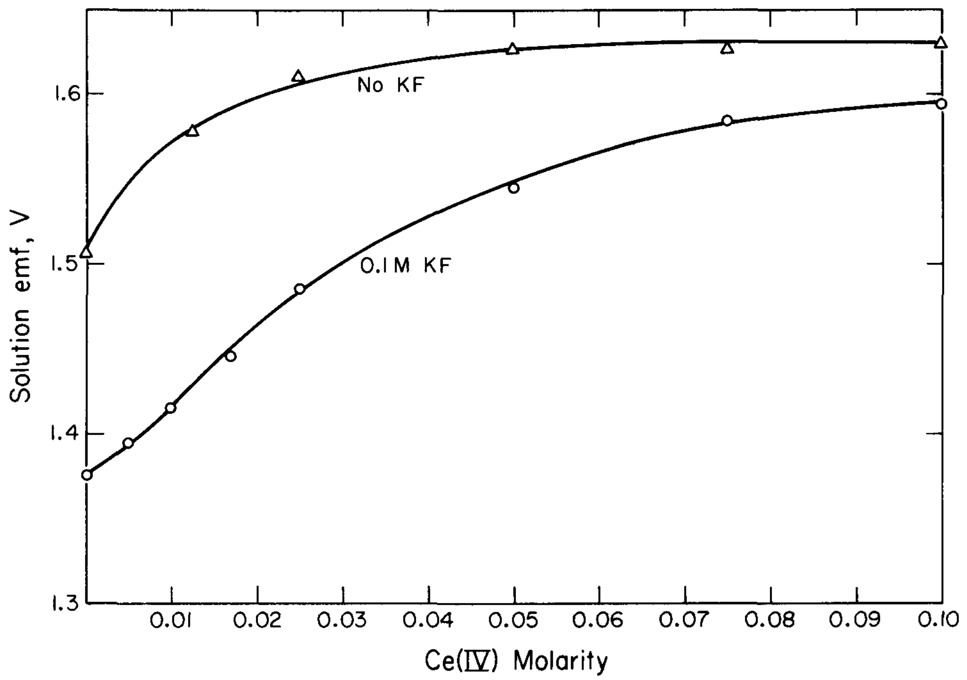

FIG. 13 EMF OF 8M HNO_3 SOLUTIONS CONTAINING Ce(IV) AND KF

The effect of increasing fluoride concentration on the emf of 8M HNO_3-0.025M Ce(IV) is illustrated in Figure 14. These data were obtained by maintaining constant HNO_3 and Ce(IV) concentrations while gradually increasing the fluoride concentration by titration. The emf of the solution decreased as fluoride increased, but no unusual behavior was observed when the optimum ratio of 2KF/Ce(IV) was reached. These experiments indicate that the observed maximum PuO_2 dissolution at 2KF/Ce(IV) is not related directly to a change in solution emf. However, it is important to note that the emf during the dissolution experiments is affected by the presence of a number of species besides Ce(IV), including Ce(III), Pu(IV), Pu(VI), and fluoro complexes of these species.

Cerium(IV)-Fluoro Complex Formation in 8M HNO_3

The PuO_2 dissolution in HNO_3-F^- solutions is dependent on the concentration of free fluoride* or uncomplexed fluoride in solution.[1,2] Thus, the amount of uncomplexed fluoride in 8M HNO_3-Ce(IV)-KF solutions was investigated to aid in the understanding of PuO_2 dissolution data.

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*In this context "free fluoride" normally means fluoride not complexed by some available metal ion, such as Al^{3+}. In high H^+ concentrations, the fluoride is present almost entirely as undissociated HF, and very little free fluoride ion exists.

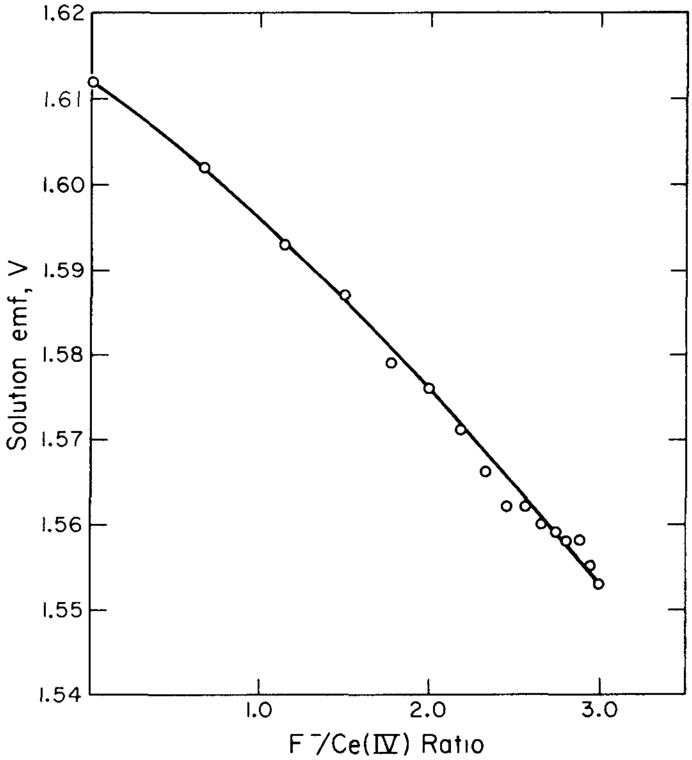

FIG. 14 EMF OF 8M HNO_3 - 0.025M Ce(IV) SOLUTIONS CONTAINING VARYING KF CONCENTRATIONS

The rapid decrease in uncomplexed fluoride as Ce(IV) increases (Figure 15) confirms that Ce(IV) strongly complexes fluoride. During dissolution experiments, the uncomplexed fluoride concentration will be even lower due to the formation of plutonium fluoro complexes. The observed slow PuO_2 dissolution in solutions with a KF/Ce(IV) ratio of 1.0 is explained by the very low uncomplexed fluoride concentrations in these solutions. There is no unusual change, however, in uncomplexed fluoride associated with solutions that gave maximum dissolution rates.

Information concerning the nature of the Ce(IV) fluoro complex species may be derived from these data by calculation of $\bar{n}$, the average ligand number. $\bar{n}$ is defined in Equation 1.

$$\bar{n} = \frac{\text{complexed fluoride}}{\text{total Ce(IV)}} = \frac{\text{total fluoride - uncomplexed fluoride}}{\text{total Ce(IV)}} \quad (1)$$

where uncomplexed fluoride is predominately undissociated HF.

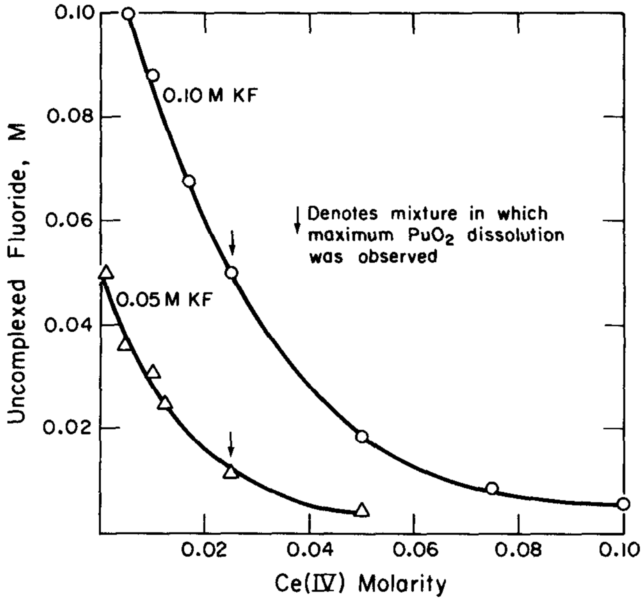

FIG. 15 UNCOMPLEXED FLUORIDE CONCENTRATIONS IN 8M HNO_3 - Ce(IV) - KF SOLUTIONS

The results of such calculations are shown in Figure 16. The total KF/Ce(IV) ratio is shown for each point; when this ratio is between 2 and 6, the major fluoro** complex species appear to be CeF_2^{2+}. At lower KF/Ce(IV) ratios there is insufficient fluoride available to completely form CeF_2^{2+}; thus, CeF^{3+} predominates. Since the rate of PuO_2 dissolution has been shown to decrease rapidly when the original KF/Ce(IV) ratio is less than 2.0, this tentatively suggests that PuO_2 dissolution is related to the CeF_2^{2+} concentration. Considerable additional study would be required to establish this relationship.

**The existence of nitrato and/or mixed fluoro-nitrato complexes is suspected; however, these data apply only to fluoro complex formation.

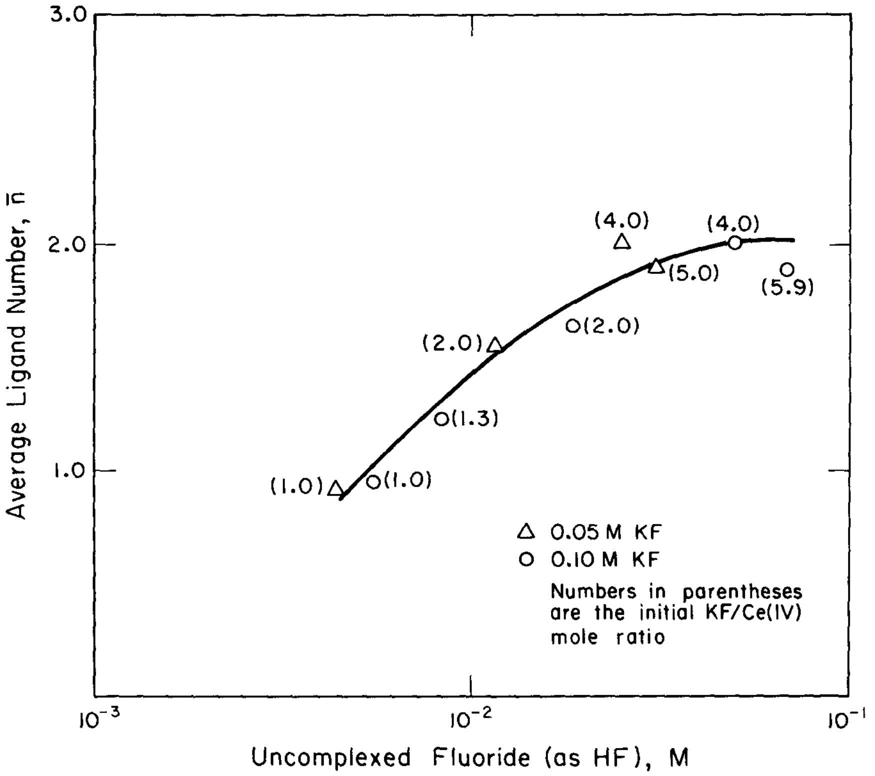

FIG. 16 Ce(IV) FLUORO-COMPLEX FORMATION IN 8M HNO_3

EVALUATION OF THE RESULTS

The effectiveness of Ce(IV), KF, and Ce(IV)-KF mixtures as promoters of PuO_2 dissolution in HNO_3 is compared in Figure 17 (8M HNO_3) and Figure 18 (4 to 15M HNO_3). Although the dissolution rate of PuO_2 in HNO_3 is increased significantly by the addition of Ce(IV), the rate increase is considerably less than that attainable with fluoride or Ce(IV)-KF mixtures. (The KF/Ce(IV) ratio determines whether KF or Ce(IV)-KF is better.) Disadvantages of Ce(IV) are (1) stoichiometric quantities are necessary for complete dissolution of PuO_2 and (2) hydrothermal precipitation of CeO_2 is possible in dilute HNO_3 solutions. Also, recent studies at ORNL[23] have shown that ruthenium catalytically reduces Ce(IV) in nitric acid; thus, Ce(IV) will be ineffective for PuO_2-UO_2 fuel dissolution when fission product ruthenium is present. The deleterious effect of ruthenium in the Ce(IV)-KF system is not known, but is expected to be less than for Ce(IV) alone because fluoride is not removed by ruthenium. In view of the ruthenium problem, HNO_3-F^- solutions appear most promising for breeder fuel processing. Nitric acid solutions containing Ce(IV) and Ce(IV)-F^- mixtures may be most useful for dissolving unirradiated PuO_2 and UO_2-PuO_2 materials, as in scrap recovery operations.

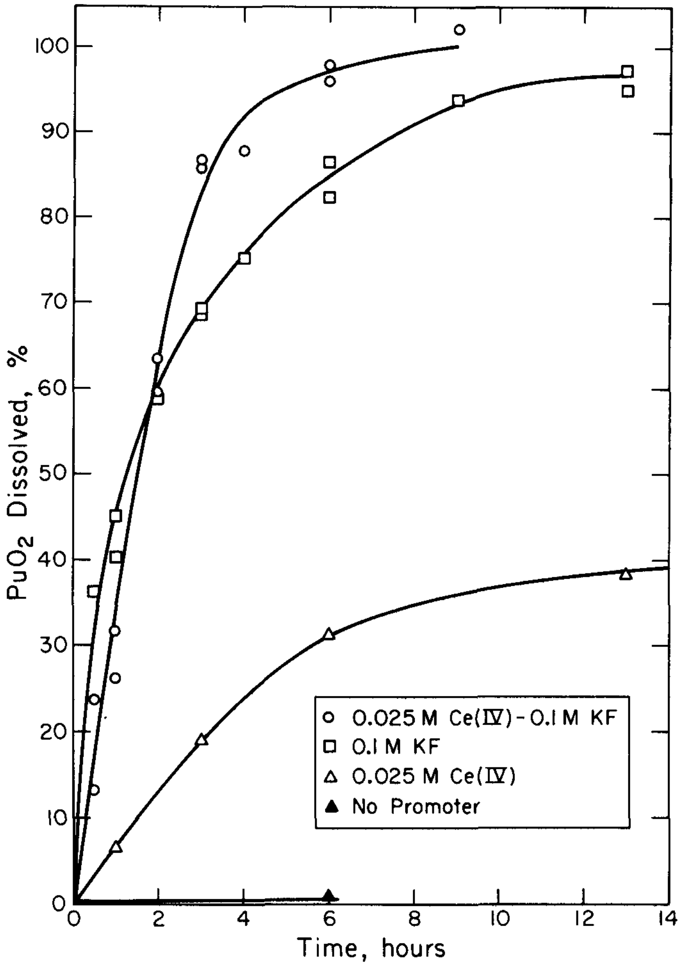

FIG. 17 DISSOLUTION OF PuO_2 IN 8M HNO_3

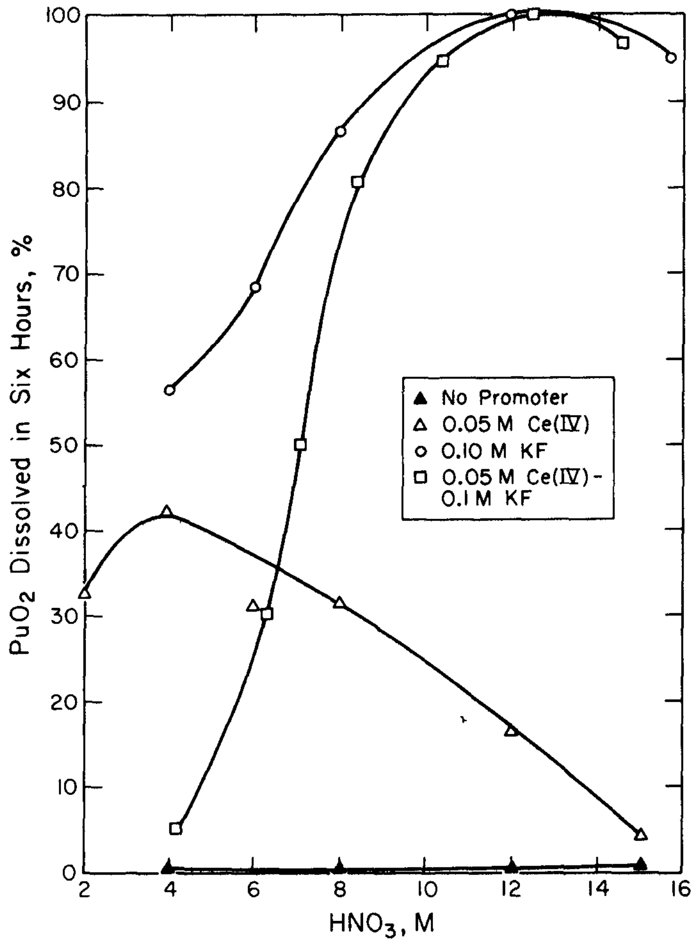

FIG. 18 EFFECT OF HNO_3 CONCENTRATION ON PuO_2 DISSOLUTION PROMOTED BY Ce(IV), KF, AND Ce(IV)-KF MIXTURES

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