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PLUTONIUM DIOXIDE DISSOLUTION IN
NITRIC/HYDROFLUORIC ACID MIXTURES -
KINETICS AND MECHANISM

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ABSTRACT

The kinetics of the fluoride-catalyzed dissolution of powdered plutonium oxide in nitric acid have been investigated over the concentration ranges of 2.0 to 12.0 molar nitric acid and 0.01 to 0.5 molar fluoride. The dissolution rate is controlled by diffusion of fluoride through a product layer on the surface of the solid PuO_2 . The thickness of this layer increases as the reaction progresses and rapidly slows dissolution. The kinetics follow the parabolic rate law, $C = Kt^{1/2}$, where C is the concentration of dissolved Pu. The constant, K, is dependent on HF and HNO_3 concentrations, surface area, the diffusion coefficient, and temperature. The kinetic data can be explained on the premise that two parallel reactions occur, one forming the unreactive surface layer and inhibiting the reaction and the other forming the soluble plutonium species.

PLUTONIUM DIOXIDE DISSOLUTION IN NITRIC/HYDROFLUORIC ACID
MIXTURES - KINETICS AND MECHANISM

INTRODUCTION

The dissolution of plutonium dioxide in nitric/hydrofluoric acid mixtures is a necessary step in reprocessing PuO_2 - containing nuclear materials. Thus far, little effort has been made to establish the mechanism of this process. Much of the knowledge of this reaction has been obtained from studies of sintered UO_2 - PuO_2 and PuO_2 fuel pellets(1-3) rather than the pure powdered oxide.

Molen(4) has studied the effect of PuO_2 /solvent ratio on the dissolution rate and found that the amount dissolved increased with increasing PuO_2 /solvent ratio. He also found that the rate was more dependent on the surface area than the mean crystallite size of the oxide. Another report(5) proposed a reaction mechanism in which the slow step is the formation of a fluoride complex of Pu.

The objective of the present work was to determine the kinetics of dissolution of PuO_2 in order to obtain a better knowledge of the mechanism. This knowledge should enable the prediction of factors which contribute to faster dissolution.

Powdered PuO_2 was used in this work rather than sintered pellets. The powdered material has the advantages of consistency of composition, lack of property variation due to pellet fabrication, and a reasonable rate of dissolution at the experimental conditions used. Since the rate of dissolution of a given sample will vary, depending on the preparative history of the oxide, the rate constants obtained in this study are applicable only to similarly - prepared oxide. However, dependence of the rate on temperature, hydrofluoric acid and nitric acid concentrations should be the same for all pure PuO_2 .

The dissolution was studied within a range of variables similar to those commonly used to dissolve PuO_2 . Nitric acid concentration was varied from 2.0 to 12.0M and HF concentration from 0.01 to 0.5M. Temperature was varied from 35.0 to 75.0 °C.

SUMMARY AND CONCLUSIONS

The kinetics of dissolution of powdered PuO_2 in nitric/hydrofluoric acid mixtures were determined. The variables studied were PuO_2 /solvent ratio, fluoride concentration, nitric acid concentration, and temperature. Under a given set of reaction conditions, the

dissolution can be described by the parabolic rate law

$$[\text{Pu}] = Kt^{\frac{1}{2}}$$

The effect of dissolution variables on K can be summarized by the equation

$$K = K_1 a_{\text{HF}} W^{\frac{1}{2}} e^{- (E_a / RT)}$$

where K_1 is the rate constant, a_{HF} is the activity of undissociated HF, W is the PuO_2 /solvent ratio, and E_a is the apparent activation energy.

The data are consistent with a mechanism in which the dissolution rate is controlled by diffusion of HF through a surface film on the oxide. This surface film grows thicker with time and rapidly slows the dissolution. The activation energy for the process is 6.0 kcal/mole which is well within the range expected for a diffusion-controlled dissolution.

EXPERIMENTAL

REAGENTS AND APPARATUS

The PuO_2 powder was obtained by burning a plutonium metal button in air. The oxide was sieved and mixed in order to ensure a uniform particle size distribution. Surface area was determined to be 2.9 m^2/g and the average particle diameter 23.4 microns. Emission spectrographic analysis of the oxide gave the following amounts of metallic impurities:

<u>Metal Impurity</u>	<u>PPM</u>
Fe	1050
Ni	785
Ta	305
Ca	190
Cr	180

Reagent grade HNO_3 (Mallinckrodt) and NaF (B & A) were used throughout. Sodium fluoride was the source of HF in the solvent matrix.

The reaction vessel was a 150 ml polycarbonate plastic cylinder surrounded by a glass water jacket. A vinyl plastic stopper fitted with a plastic coated thermometer and polypropylene sampling tube was fitted to the top of the cylinder. The reaction mixture was thermostated to ± 0.2 °C by circulating water through the jacket with a Haake E-51 constant temperature circulator. The jacket was placed on a magnetic stirrer and a teflon stir-bar was used to agitate the mixture. In order to prevent contamination with silica and loss of HF, the solvent and reaction mixtures were contained in plastic at all times.

Time was measured with a stopwatch.

PROCEDURE

Fifty milliliters of the HNO_3/HF mixture was used in each experiment. The HNO_3 was brought to the proper temperature and a weighed amount of NaF added and dissolved. A known mass of PuO_2 ($\pm 0.01\text{g}$) was then added with rapid stirring to begin the dissolution. Samples of the suspension were withdrawn through the polypropylene tube into a plastic syringe and rapidly filtered through a 0.25μ "Solvinert" filter membrane (Millipore Corp.) contained in a syringe filter holder. The total time needed for sampling was about 20 seconds and the first sample was taken after two minutes.

Plutonium concentrations in the samples were determined by alpha counting. Total fluoride concentrations were determined by diluting the samples with a total ionic strength adjustment buffer (TISAB, Orion Research Inc.) and then measuring the fluoride with an Orion fluoride combination electrode.

It was found that the dissolution was slower if part of the oxide was not suspended in the solvent. To eliminate stirring rate as a variable, rapid stirring was used, with all of the oxide suspended in the solvent.

RESULTS AND DISCUSSION

ANALYSIS OF RATE CURVES

Examples of several dissolution curves are shown in Figure 1. The reaction begins with a relatively high dissolution rate and then rapidly slows. This dramatic decrease in the dissolution rate with time cannot be explained by a decrease in surface area due to contracting particle size. According to Solntsev and Tolmachev⁽⁶⁾, chemically controlled dissolutions of monodisperse powders are consistent with the relationship.

$$m_0^{1/3} - m_t^{1/3} = kt \quad (1)$$

where m_0 is the initial mass of PuO_2 , m_t the mass after time t , and k is a rate constant. Plots of $(m_0^{1/3} - m_t^{1/3})$ versus t did not approach linearity. Therefore, the dissolution is diffusion controlled.

Since the reaction mixture is vigorously stirred, it seems unlikely that diffusion of reactants through the liquid is the controlling factor. As long as all the oxide is suspended in solution, changes in the stirring speed did not affect the rate. Evidently, a film is formed on the surface of the oxide which grows with time and inhibits the reaction. The growth of this film is given by the parabolic equation

$$x = kt^{1/2} \quad (2)$$

where x is the thickness of the film and k is the rate constant. The rate of transport dM_y/dt of the diffusing species across the film is⁽⁷⁾

$$\frac{dM_y}{dt} = \frac{DC_y}{x} \quad (3)$$

where D is the diffusion coefficient and C_y is the concentration of the diffusing species in solution. The change in Pu concentration in solution is proportional to dM_y/dt

$$\frac{d[Pu]}{dt} = \frac{k' DC_y}{x} \quad (4)$$

Substituting (2) into (4) and integrating

$$[Pu] = \frac{k' DC_y}{2k} t^{\frac{1}{2}} \quad (5)$$

$$\text{or} \quad [Pu] = K t^{\frac{1}{2}} \quad (6)$$

at constant C_y .

Plots of $[Pu]$ versus $t^{\frac{1}{2}}$ for several experiments are shown in Figure 2. These curves are linear with slopes equal to K . Equation (6) was found to describe all the dissolution data, the value of K depending on HF and HNO₃ concentrations, oxide/solvent ratio, and temperature. It should be pointed out that only about 20 percent or less of the oxide was dissolved in most of these experiments. Equation (6) does not take into account the decrease in the surface area of the reactive interface with time and therefore does not represent the reaction kinetics in the later stages of dissolution. A summary of the kinetic data is given in Table I.

The intercepts of the lines in Figure 2 are not exactly at the origin. This may be due to a small induction period before dissolution begins.

EFFECT OF PuO₂/SOLVENT RATIO

As shown in Figure 2, dissolution rates are dependent on PuO₂/solvent ratios. The dissolution rate is proportional to the surface area (or concentration of reactive sites) of the oxide and is therefore proportional to the PuO₂/solvent ratio. According to equation (6), the rate, in terms of $d[Pu]/dt$, is given by

$$\frac{d[Pu]}{dt} = \frac{K^2}{2[Pu]} \quad (7)$$

Therefore, the $\text{PuO}_2/\text{solvent}$ ratio should be proportional to K^2 . Figure 3 shows that this is true. In this plot K^2 is corrected for HF adsorption. At higher $\text{PuO}_2/\text{solvent}$ ratios more HF is adsorbed from solution and since K is proportional to $[\text{HF}]$ (see below) the value of K will decrease accordingly.

TABLE I

SUMMARY OF KINETIC DATA

<u>Run #</u>	<u>$\text{PuO}_2/\text{Solvent}$ Ratio, g/l</u>	<u>$[\text{HF}], \text{M}$</u>	<u>$[\text{HNO}_3], \text{M}$</u>	<u>Temp., °C</u>	<u>$K, \text{g/l/min.}^{\frac{1}{2}}$</u>
3	200	0.048	10.0	35.0	1.81
2	100				1.57
5	40				1.20
6	20				0.80
7A	100	0.012			0.15
8A		0.024			0.68
28		0.036			1.23
12		0.048			1.52
27		0.072			2.23
9A		0.095			3.06
26		0.048	12.0		2.40
23			8.0		1.15
24			6.0		0.69
25			4.0		0.50
19			10.0	45.0	2.16
20				55.0	2.88
21				65.0	3.04
22				75.0	4.10

EFFECT OF HF CONCENTRATION

Calcined PuO_2 dissolves extremely slowly in pure nitric acid. Addition of small amounts of HF greatly speeds the dissolution. The action of the fluoride is definitely catalytic since each mole of HF will dissolve many times as many moles of PuO_2 . The dependence of K on $[\text{HF}]$ is shown in Figure 4. The constant, K , is directly proportional to HF concentration. This means that the dissolution rate is controlled by the diffusion of fluoride species through the surface film on the oxide. Under the conditions of high acid and low fluoride concentrations used in these experiments, the HF species will greatly predominate with very small amounts of F^- and HF_2^- . It therefore seems likely that undissociated HF is the diffusing species. Additional evidence to support this idea is given in the next section.

The concentration of total fluoride, $[\text{HF}]_t$, in the aqueous phase was measured as a function of time in order to see if appreciable amounts of fluoride were adsorbed on the surface of the oxide. The results illustrated in Figure 5 show that only small amounts of fluoride are adsorbed. Additional measurements show that the amount adsorbed is not sensitive to $[\text{HF}]_t$. The $K = 0$ intercept in Figure 4 is due to adsorption of HF from solution. The amount adsorbed (0.25 mmole) is approximately the same for runs with equal PuO_2 /solvent ratios.

Figure 5 also shows that fluoride is desorbed after the initial adsorption. Because of this observation, it seems unlikely that the surface layer is a plutonium fluoride compound. Plutonium fluoride can, however, be precipitated if the initial $[\text{HF}]_t$ is too great.

EFFECT OF HNO_3 CONCENTRATION

Since the dissolution rate is controlled by diffusion of HF through the surface layer, the effect of changing the HNO_3 concentration must be to either change the concentration or activity of the HF or change the thickness or composition of the layer. Figure 6 shows a rapid increase in K with increasing total HNO_3 concentration, $[\text{HNO}_3]_t$.

This intensified reactivity of HNO_3 /HF mixtures with increasing $[\text{HNO}_3]_t$ has been generally observed in dissolution of metals and in the dissolution of ThO_2 (8). Vdovenko *et al.* (9), attribute this behavior to a sharp increase in the activity of HF as the $[\text{HNO}_3]_t$ is raised. They have measured activity coefficients for undissociated HF in mixtures up to 6.6 molar HNO_3 . Values for the activity coefficient from (9) and some extrapolated values at higher $[\text{HNO}_3]_t$ are given in Table II.

TABLE II

ACTIVITY COEFFICIENTS* FOR HF IN HNO_3 AT 25 °C

$[\text{HNO}_3]_t$	γ_{HF}
4.0	2.5
6.0	3.5
8.0	5.3
10.0	7.8
12.0	10.2

* $\gamma_{\text{HF}} = a_{\text{HF}}/N_{\text{HF}}$ where N_{HF} is the mole fraction of HF.

These activity coefficients were used in calculating activities of HF in the above concentrations of total HNO_3 . Estimates of the activity coefficients at 35 °C were only a few percent different than above values and are therefore expected to be near the real values at 35 °C. A plot of K as a function of HF activity, a_{HF} , is given in Figure 7. The data points give a linear curve with the intercept, as expected, at the origin. The constant, K, can therefore be described in terms a_{HF} . This gives added proof that the dissolution is controlled by diffusion of undissociated HF alone. The increase in activity of HF as HNO_3 concentration is raised can be explained by a decrease in the interaction of HF with water molecules (hydration and dissociation).

EFFECT OF TEMPERATURE

Kinetic runs were made from 35 °C to 75 °C (the limits of the apparatus). Increasing the temperature greatly speeded the dissolution. The activation energy, E_a , for the diffusion process calculated from the slope of the plot of $\ln K$ versus $1/T$ (Figure 8) is 6.0 kcal/mole. This is well within the range of E_a values expected for diffusion processes. A dissolution controlled by a surface reaction would be expected to have a higher E_a .

RATE LAW

Under a given set of experimental conditions the dissolution of PuO_2 has been shown to be described by equation (6). The effects of the PuO_2 /solvent ratio, fluoride and acid concentrations, and temperature on K have been determined. Combining the data from all these observations gives the expression for K.

$$K = K_1 a_{\text{HF}} W^{\frac{1}{2}} e^{-(E_a/RT)}$$

where K_1 is the rate constant, a_{HF} the activity of HF, W the PuO_2 /solvent ratio, and E_a the apparent energy of activation.

PROPOSED DISSOLUTION MECHANISM

A mechanism consistent with the data obtained is:

- (Step 1) - Formation and growth of a protective surface layer.
- (Step 2) - Diffusion of undissociated HF through the layer to a reaction interface.
- (Step 3) - Reaction of the HF to form a soluble Pu species at the interface.
- (Step 4) - Diffusion of the soluble Pu species through the surface layer to the solution.

Step 2 is the rate controlling step. Unfortunately no information concerning the composition or formation of the activated complex for Step 3 can be gained from the kinetic data.

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FIGURE I DISSOLUTION CURVES AT SEVERAL PuO₂/SOLVENT RATIOS, W, g/l

FIGURE 2 PLOTS OF [Pu] VERSUS T^{1/2} FOR RUNS OF DIFFERENT PuO₂/SOLVENT RATIO'S, W

FIGURE 3 PLOT OF PuO₂/SOLVENT RATIO VERSUS K² (CORRECTED FOR HF ADSORPTION)

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FIGURE 4 DEPENDENCE OF K ON INITIAL HF CONCENTRATION

FIGURE 5 ADSORPTION OF FLUORIDE FROM SOLUTION DURING DISSOLUTION

FIGURE 6 DEPENDENCE OF K ON HNO_3 CONCENTRATION

FIGURE 7 DEPENDENCE OF K ON THE ACTIVITY OF UNDISSOCIATED HF AT DIFFERENT HNO_3 CONCENTRATIONS

FIGURE 8 DEPENDENCE OF K ON TEMPERATURE