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THE ELECTROLYTIC DISSOLUTION OF
PLUTONIUM IN NITRIC ACID

THE DOW CHEMICAL COMPANY
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THE ELECTROLYTIC DISSOLUTION OF PLUTONIUM IN NITRIC ACID

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Frend J. Miner

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The Electrolytic Dissolution of Plutonium in Nitric Acid

James W. Berry and Frend J. Miner

Abstract. The rate of dissolution of plutonium metal in nitric acid-fluoride systems using electrolysis was determined as a function of nitric acid concentration, fluoride concentration, and current density. Other parameters investigated included type of current and type of metal.

The optimum conditions for rapid dissolution were found to be high nitric acid concentration (15.0M) and a high applied current (10 amp). Fluoride concentration, over the range investigated (0.01M to 0.13M), was found to have little effect on the dissolution rate, although its presence is necessary.

Analysis of the off-gases showed the hydrogen concentration to be near background concentration.

INTRODUCTION

Purification of plutonium metal is carried out at Rocky Flats by an anion exchange method. This requires the plutonium to be in 7.0M nitric acid. In the past, plutonium has been dissolved in hot concentrated nitric acid containing fluoride. This method occasionally resulted in fires and explosions which were attributed to hydrogen.

Recently the plutonium has been oxidized (burned) to plutonium dioxide and then dissolved in a nitric acid-fluoride solvent. This process is slow.

Earlier work has been done on the electrolytic dissolution of plutonium (1). From the results of that work it appeared possible to optimize the conditions and rapidly and safely dissolve plutonium metal directly in nitric acid.

The objective of this project was to determine the optimum conditions for the electrolytic dissolution of plutonium in nitric acid.

EXPERIMENTAL

Apparatus: The dissolver system, Figure 1, consisted of a 600-ml stainless steel beaker in which

the sample could be immersed on a tantalum rod. The tantalum rod served as an anode connector to the sample and the beaker served as the cathode. A water bath surrounded the lower portion of the beaker and was used to control the temperature. The solvent volume was 200 ml and was stirred constantly during dissolution. Direct current was supplied from a full wave rectifier having a maximum capacity of 10 amp.

Samples: Samples used for the preliminary investigations were flat, irregular-shaped pieces of either alloyed or unalloyed plutonium. The alloy was Pu-1 wt % gallium. Each sample had a hole drilled through the middle so that the sample could be attached to the tantalum rod.

For the experiments in which the optimum conditions were determined, a cylindrical rod was cast from unalloyed plutonium. The casting was then machined on the outside surface and a hole was drilled down through the center. Discs were cut from the cylinder

Figure 1. Electrolytic dissolver.

and the discs were degreased with alcohol. Each disc had a surface area of 20 cm² and weighed 15 grams.

Procedure: Each sample was weighed and then attached to the tantalum rod (anode) using a tantalum nut on each side of the sample. The sample was immersed in the test solution and current was supplied. After the required time, the current was turned off, the samples were washed with distilled water, air dried, and re-weighed. If duplicate runs were made, the same sample and the same solution was used and the procedure repeated. During dissolution, ice cubes were added to the water bath to maintain the temperature of the solvent at 23°C.

SUMMARY AND CONCLUSIONS

The rate of dissolution of plutonium in greater than 5.0M nitric acid concentrations can be increased significantly by the addition of a slight amount of fluoride while applying a direct current to the plutonium metal. (Below 5.0M concentration rapid dissolution can be obtained without electrolysis (2,7).

The effect of the nitric acid concentration is less significant than the current on the rate of dissolution. Fluoride concentration has little effect on the dissolution rate although its presence is necessary. Absence of fluoride results in an extremely slow dissolution rate.

Within the ranges investigated, the fastest rate of dissolution was obtained with 10 amp, 15.0M nitric acid, and 0.01M HF.

With the experimental equipment and conditions used, the following effects were observed: direct current was more effective than alternating current; lower acid concentrations dissolved alloyed metal approximately 30% faster than unalloyed metal; in 10.0M HNO₃, and above, the dissolution rates of the two metals were equal; and very little evolved hydrogen could be detected.

If the dissolution was only electrolytic, the applied current would be the only parameter which affected

the dissolution rate. It would then be possible to calculate current efficiencies. Control of the current would also be a very convenient way to control the rate of dissolution. This, however, is not the case. Parameters such as acid concentration and current density do affect the rate of dissolution; indicating that some chemical dissolution is taking place.

RESULTS AND DISCUSSION

Preliminary Investigations:

COMPOSITION OF EVOLVED GASES – The first experiments on the dissolution of plutonium by electrolysis were designed to give a qualitative and quantitative measure of the off-gases. If the dissolution is a simple hydrogen ion displacement, i.e.,

an explosive atmosphere could easily be created by the presence of hydrogen.

Gas chromatography was used for the analyses of the off-gases (3). Acid concentration, applied current, temperature, and type of metal were varied. Through the ranges of conditions investigated, i.e., 5.0 to 15.0M nitric acid, 23 to 70°C, 0 to 10 amp, and alloyed compared with unalloyed metal, the hydrogen did not approach a hazardous concentration [approximately 4% hydrogen (4)]. A typical composition consisted of 0.1% to 0.3% hydrogen and about 0.1% nitrous oxide. The major concentrations detected were oxygen, carbon dioxide, and nitrogen.

Other investigators (5) have reported a typical concentration of 0.3% in off-gases from the electrolytic dissolution of power reactor fuels.

DIRECT CURRENT COMPARED WITH ALTERNATING CURRENT – The relative effectiveness of direct current and alternating current on the rate of dissolution was examined. Table I shows that direct current is more effective than alternating current under the conditions investigated.

The same samples of both alloyed and unalloyed metal were used for both AC and DC. Both samples were approximately the same size.

An experiment in which the plutonium was made the cathode and direct current was applied resulted in a very low dissolution rate.

Table I. Effect of alternating current and direct current on the rate of dissolution.

Solvent - 10M HNO ₃ , 0.07M HF Time - 10 minutes			
Type of Metal	Type of Current	Current Applied (amp)	Pu Dissolved (grams)
Unalloyed	ac	5	0.4957
Unalloyed	dc	5	2.1163
Alloyed	ac	5	0.4715
Alloyed	dc	5	2.1450

UNALLOYED PLUTONIUM COMPARED WITH Pu-1 wt % Ga - The type of metal only affected the dissolution rate at lower concentrations of nitric acid. In 5.0M HNO₃-0.07M HF, at 10 amp, the alloy dissolved about 30% faster than the unalloyed metal. However, when the nitric acid concentration was increased to 10.0M, the difference in the rate of dissolution was within the experimental error of $\pm 5\%$.

CURRENT DENSITY - The effect of current density was studied by two methods. In the first method the applied current was held constant and the surface area was varied. Although current density varied inversely with respect to surface area, the total plutonium dissolved in a given time did not vary appreciably. However, when the applied current was increased and the surface area held constant, the total dissolution rate of plutonium increased. Table II summarizes the results.

Table II. Effect of current density on rate of dissolution.

Applied Current (amps dc)	Surface Area (cm ²)	Current Density (amp/cm ²)	Pu Dissolved (grams/10 min.)
10	6.4	1.56	2.99
10	12.8	0.78	2.87
10	20.0	0.50	3.04
5	20.0	0.25	1.55
0	20.0	0.00	0.71

Optimizing Conditions:

Based on data gained, a factorial experiment was set up to determine conditions that would give the optimum rate of dissolution. A second-order rotatable

design was used for this experiment (6). This particular design allows three parameters to be investigated at three levels using only thirteen experimental determinations, rather than the twenty-seven required by a full factorial design.

Table III shows the parameters and levels chosen for study.

Table III. Parameters and levels studied.

Parameter	Levels
Nitric Acid Concentration	5.0M, 10.0M, 15.0M
Fluoride Concentration	0.01M, 0.07M, 0.13M
Current (dc)	0 5amp, 10 amp

Figure 2 shows graphically the main effects of the three parameters. The curves were obtained by averaging the results for a single condition. That is, the indicated rate for 5.0M HNO₃ was obtained by averaging the rates at different current levels and fluoride levels and the 5.0M HNO₃ level.

The curves in Figure 2 indicate that the effect of current, compared with the effect of fluoride, has the most significant effect on the rate of dissolution.

The curves in Figure 3 show the effect of the interactions between any two parameters. These results were also obtained by averaging the rates at all levels of the third parameter, i.e., the point for 5.0M HNO₃-0.01M HF is an average of the dissolution rates for these two conditions at 0, 5, and 10 amp. The predominant interaction is between nitric acid and current.

Experimental results and statistical data for the conditions are reported in the Appendix.

In all preliminary experiments solvent temperatures were not controlled and a residue remained in the solution. This residue was found to be readily soluble in hot, 7M nitric acid. Dissolutions in which temperatures were controlled near 23°C, resulted in solutions that were free of residue.

The optimum conditions were found to be high nitric acid concentration (15.0M), high applied current (10 amp), and solvent temperature of 23°C.

Figure 2. Main effects of parameters on dissolution rate.

Figure 3. Interaction between parameters on dissolution rate.

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APPENDIX

Data from Factorial Experiment: A three by three factorial experiment was arranged on a second-order rotatable design (6). Dissolution rates were measured for thirteen of the possible twenty-seven conditions and the remaining fourteen rates were calculated. In all cases duplicate dissolutions were measured over ten-minute periods, except for the "center point" of the design (10.0M HNO_3 , 0.07M HF, and 5 amp) where seven runs were made, and the average value used in the calculations.

Table A-I shows the dissolution rates of the various combinations of parameters and levels.

Table A-II, by the relative magnitude of the mean square, shows the importance of each main effect and

Table A-II. Analysis of variance.

Source of Variation	Degrees of Freedom	Mean Square
X_1 (HNO_3)	2	51.541046
X_2 (HF)	2	1.231923
X_3 (current)	2	749.639773
$X_1 X_2$	4	0.066068
$X_1 X_3$	4	40.917669
$X_2 X_3$	4	0.204951
$X_1 X_2 X_3$	8	0.000093

each interaction in comparison with one another. The larger the number, the greater is the effect.

Table A-III is the average dissolution rates from which Figures 2 and 3, of the text, were plotted.

Table A-I. Dissolution rates from optimization experiment.

Values are dissolution rates in $\text{mg}/\text{cm}^2/\text{min}$.

Current	Nitric Acid Concentration								
	5.0M			10.0M			15.0M		
	Fluoride Concentration			Fluoride Concentration			Fluoride Concentration		
	0.01M	0.07M	0.13M	0.01M	0.07M	0.13M	0.01M	0.07M	0.13M
0 Amp	3.269	3.551*	3.996	0.0797*	0.284	0.956*	0.285	0.103*	0.694
5 Amp	7.766*	8.372	8.327*	8.0062	8.584 ⁺	8.716	12.456*	12.598	12.700*
10 Amp	13.984	15.223*	14.995	17.349 *	18.510	18.510*	25.738	26.513*	26.432

* Average of two experimental values. Other values have been calculated by least squares fit of a second degree polynomial (6).

+ Average of seven experimental values.

Table A-III. Main effects and interactions.

Main effect of X_1 (nitric acid concentration).

5.0 <u>M</u>	8.831925 mg/cm ² /min
10.0 <u>M</u>	8.999674
15.0 <u>M</u>	13.058171

HNO₃HF

15.0	0.07	13.071954
15.0	0.13	13.275785

Main effect of X_2 (hydrofluoric acid concentration).

0.01 <u>M</u>	9.881689
0.07 <u>M</u>	10.415877
0.13 <u>M</u>	10.592205

Interaction of nitric acid concentration and current.

5.0	0	3.605931
5.0	5	8.155292
5.0	10	14.734551
10.0	0	0.439996
10.0	5	8.435953
10.0	10	18.123074
15.0	0	0.361223
15.0	5	12.585141
15.0	10	26.228151

Main effect of X_3 (current)

0 Amp	1.469050
5 Amp	9.725462
10 Amp	19.695258

Interaction of nitric and hydrofluoric acid concentration.

<u>HNO₃</u>	<u>HF</u>	
5.0	0.01	8.339977
5.0	0.07	9.049309
5.0	0.13	9.106488
10.0	0.01	8.478314
10.0	0.07	9.126369
10.0	0.13	9.394341
15.0	0.01	12.826775

Interaction of hydrofluoric acid concentration and current.

0.01	0	1.211514
0.01	5	9.409612
0.01	10	19.023940
0.07	0	1.313068
0.07	5	9.852156
0.07	10	20.082407
0.13	0	1.882569
0.13	5	9.914618
0.13	10	19.979428