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**INVESTIGATION OF THE ELECTROLYTIC
DISSOLUTION OF PLUTONIUM**

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Chemistry Research and Development
PROCESS CHEMISTRY AND ENGINEERING

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INVESTIGATION OF THE ELECTROLYTIC DISSOLUTION OF PLUTONIUM

Robert P. DeGrazio and Frend John Miner

Abstract. Experiments have shown that it is possible to dissolve plutonium electrolytically in a nitric acid solution. Parameters such as current density and electrolyte composition have been investigated and are discussed. Also included are suggestions for future work.

HISTORY

The work described in this report was classified when it was originally reported in January 1963. Declassification rulings that have occurred since that time now make this work unclassified. No additional work has been done since the 1963 report, and no content changes have been made in issuing this report.

INTRODUCTION

The possibility of dissolving metallic plutonium by electrolytic means was investigated in the early months of 1962. The approach taken was to immerse two strips of plutonium in concentrated HNO_3 . One strip was the anode, the other was the cathode. Electrical connections were made by means of alligator clips. A 15-ampere DC power supply was used as the source of current. It was possible to dissolve 50 g of metal in 2 hours using 10 amps of current; however, the resulting solution was cloudy, which indicated particles in suspension. In addition, the plutonium became hot at the point of contact between the alligator clips and the plutonium metal.

A literature search was made to determine if any work had been done on electrolytic dissolution of plutonium. No references relative to plutonium were found. There was considerable information in the literature, however, on the electrolytic dissolution of nuclear fuel elements clad with stainless steel or zirconium.¹⁻⁷ In the cases cited, the material to be dissolved was made the anode, and the cathode was

made of some inert metal. A decision was made to investigate this type of electrode configuration for the dissolution of plutonium.

EXPERIMENTAL WORK

Laboratory Scale Work

In the first experiment, a platinum basket containing pieces of plutonium metal served as the anode. A platinum crucible served as the cathode. The electrolyte was $2M \text{HNO}_3$, and electrolysis was conducted for 5 minutes at 2 amperes. Using this system, the amount of plutonium dissolved was too low to be useful.

In the next experiment, the platinum-basket anode was replaced by a strip of tantalum to which a piece of plutonium was attached. The strip of plutonium was approximately 1-inch long, 0.5-inch wide and 0.06-inch thick. About half of the plutonium metal was submerged in the electrolyte, which was again $2M \text{HNO}_3$. With a current density of 2 A/cm^2 , the plutonium was dissolved at the rate of approximately 100 mg/min. A precipitate (or residue) was produced that was identified by X-ray diffraction as PuO_2 . Subsequent work showed that if fluoride were present, the formation of this precipitate could be prevented.

A third dissolution procedure also was investigated. The equipment and procedures were the same as previously described. The difference was that dilute NaOH was used as the electrolyte in place of HNO_3 . It was postulated that a hydroxide-type precipitate would be formed that would be soluble in acid. Dissolution was slow, however. Also, a large amount of precipitate was formed. Most of the precipitate was soluble in HNO_3 , but a black crystalline residue remained. The black precipitate was not identified.

Kilogram Scale Work

On the basis of results obtained from the laboratory scale work, the equipment was scaled up to evaluate the process for dissolving kilogram quantities of plutonium.

The electrolysis cell for the kilogram scale work was constructed from 0.05-inch-thick tantalum metal. The cell was 8 inches in height and 5.25 inches in diameter. These dimensions were limited by nuclear safety criteria. A 2-inch-long tantalum rod that was 0.5 inch in diameter was welded to the side of the electrolysis cell. Electrical connections were made to this rod with a stainless steel connector in such a manner that the tantalum container served as the cathode. A tantalum rod that was 12 inches long and 0.5 inch in diameter was used as the anode. Again, electrical connections were made with a stainless steel connector. The end of the anode rod was threaded, and a hole was drilled through the plutonium button, which was then held onto the rod by a tantalum nut.

The electrolysis cell, which was placed on top of a magnetic stirrer, and the anode rod were clamped to a ring stand for stability. An argon purge, directed down into the cell, was used to dilute any hydrogen accumulation if indeed hydrogen was generated during the reaction. Insulation was used as required to prevent electrical shorts. Power was supplied from a DC source that provided 0-15 volts and 0-50 amps.

One plutonium button, weighing 1.08 kg, was used for all of the experiments. The entire button was immersed in the electrolyte during electrolysis.

RESULTS AND DISCUSSION

Laboratory Scale Work

After conditions had been found that would permit dissolution of metallic plutonium without the formation of a precipitate, runs were made at various HNO_3 concentrations to determine the influence of acid concentration on the amount of

TABLE 1. Effect of Concentration of Nitric Acid on Amount of Plutonium Dissolved

Initial HNO_3 Concentration (M)	Pu Dissolved (g/hr)
2	7.1
5	8.6
8	8.0
10	8.7
13	10.0
16	18.6

Note: All solutions approximately 0.1M HF.
Current density in all runs approximately 1 A/cm².
Electrolysis time was 10 minutes at each acid concentration.

plutonium dissolved. The small plutonium coupons used for each run came from a single large strip of delta plutonium. About half of the coupon was submerged in the electrolyte, which was 20 ml of the HNO_3 concentration to be studied. It was made approximately 0.1M in HF. The current was adjusted so that a current density of about 1 A/cm² was used in all runs. The area of plutonium submerged was approximately 2.8 cm² in all but the final run (16M HNO_3). The area submerged in that run was approximately 5.3 cm². The results of the runs are shown in Table 1.

The amount of plutonium dissolved was determined by weighing the coupon before and after electrolysis. The data in Table 1 are from one run at each acid concentration.

The following observations were made in the course of the laboratory scale experiments:

1. The rate of dissolution is a function of current density. The data given in Table 1 resulted from use of the highest current available from the current source used (a battery charger). When that current was reduced, the rate of dissolution was likewise reduced.

2. The rate of dissolution is also a function of the HNO_3 concentration of the electrolyte.
3. A precipitate (or residue) is formed unless fluoride is present during electrolysis. Preliminary work indicates that if a precipitate is formed (because fluoride is absent), the precipitate can be dissolved by adding HF and (a) heating the solution to at least 90°C on a hot plate or (b) reversing the polarity of the electrodes and passing a current between the electrodes.
4. An electrical resistive coating (presumably plutonium oxide) forms on the plutonium surface. If the current is turned off before dissolution is completed, the coating must be scraped off before current will again flow. The higher the HNO_3 concentration, the faster the formation of this coating. Using a larger power source in the kilogram scale work, it was found that the coating did not have to be removed so carefully. This resulted, probably, from the availability of a higher voltage that overcomes initial resistance.
5. The production of oxides of nitrogen increases as the HNO_3 concentration in the electrolyte increases. White fumes (composition unknown) are evolved when using acid concentrations lower than $7.5M$.
6. Good stirring is essential for maximum dissolution efficiency.

Kilogram Scale Work

Results from the laboratory scale work indicated that the higher the concentration of HNO_3 in the electrolyte, the greater the rate of plutonium dissolution. The data also indicated that if HF is present in the electrolyte during the dissolution, a precipitate does not form. On the basis of this information, equipment was designed for kilogram

scale work to investigate the potential of the process for production use.

The electrolyte used for the kilogram scale work was concentrated HNO_3 ($15.6M$) in either $0.2M$ or $0.1M$ in HF. One button weighing 1.08 kg was used in all of the runs. The data obtained from those runs are given in Table 2.

New electrolyte was used for each of the first four runs. In Runs 5 and 6, the same electrolyte was used. In these last two runs, a smaller volume of electrolyte was used than in the previous runs. The objective was to determine how high a concentration of plutonium could be obtained. This volume was just sufficient to cover the plutonium button. New electrolyte had to be added periodically during the electrolysis to replace that which boiled off.

The current density used, 0.21 to 0.24 A/cm^2 , was the maximum available from the power supply.

In all of the runs, electrolysis was continued approximately 25 minutes. The reaction was then stopped to permit clearing the box of any hydrogen that might have been generated. This was done as a safety precaution even though work at Savannah River indicates that hydrogen is a minor constituent (less than 2%) of the cathode gas originating from a tantalum cathode in an electrolysis cell containing $10M \text{ HNO}_3$ as the electrolyte.⁷

The original weight of the plutonium button was 1080 g. After completing all of the runs, the button weighed 480 g. This would indicate that 600 g of plutonium would be in solution. There is an apparent discrepancy, however. If the value in the "Final Pu Concentration" column for each run in Table 2 is multiplied by the "Initial Volume" value for each run*—and the grams of plutonium obtained are summed—the final result indicates that 966 g of plutonium should be in solution. The discrepancy between this value and the 600 g originates from the fact that the final volume of the solution, on which

*For Run 6, use only the value of 800 from the "Final Pu Concentration" column to multiply by the initial volume of 350 ml.

TABLE 2. Kilogram Scale Electrolysis Data^a

Run No.	Electrolyte				Electrolysis Time (min)
	Initial Volume (ml)	Initial HF Concentration (M)	Final Pu Concentration (g/l)	Final H ⁺ Concentration (M)	
1	500	0.2	97	13.4	10
2	500	0.2	203	12.4	20
3	450	0.2	226	12.2	25
4	800	0.2	306	—	40
5	350	0.1	540 ^b	—	83
6	350	0.1	550 ^b 800 ^b	— —	128

a. Electrolyte. Initially 13.4M HNO₃ and noted HF concentration
Current Density: 0.21-0.24 A/cm²

b. At a plutonium concentration of approximately 550 g/l.
Pu(NO₃)₄ · 5H₂O (determined by X-ray diffraction)
precipitated in samples submitted to the laboratory for
assay although no precipitation was observed in the bulk
of the electrolyte itself. A much larger sample (about 20
ml) was taken from Run 6 and was analyzed before a
precipitate formed. This gave the 800 g/l value.

the plutonium concentration was determined, was less than the initial volume. This reduction was due to the loss of electrolyte by boiling during electrolysis. The importance of this loss and its effect on material balance calculations was not recognized until the work was completed.

It was observed that the plutonium dissolved preferentially from the top and bottom surfaces of the button. Craters were formed on the bottom surface. It was believed that this preferential dissolution was related to the stirring.

Using data from Run 4, and assuming an anode reaction [Pu → Pu(IV) + 4 electrons], there is an electrical current efficiency of 471 percent. If the anode reaction is Pu → Pu(III) + 3 electrons, the current efficiency is 356 percent. These data would indicate that a dissolution process other than electrolytic dissolution predominates; the most obvious other dissolution process is chemical.

CONCLUSIONS

The data discussed in this report, although only from introductory work, indicate that it may be practical to use the electrolytic process to dissolve metal on a production basis. Much more investigative work needs to be done.

FUTURE WORK

The following thoughts are suggestions for future work:

1. Redesign the cell to
 - a. accommodate larger and more irregular pieces of plutonium and to permit easy removal of these pieces from the cell.
 - b. provide a means for cooling the electrolyte below its boiling point and thus prevent excessive losses.

- c. permit easy removal of the plutonium solution from the cell.
2. Measure the amount of hydrogen generated. If this is excessive (and from the work previously discussed, an excess is not anticipated), proper means for safe disposal of the hydrogen would have to be designed.
3. Design a rapid and safe means of removing the oxides of nitrogen generated during electrolysis.
4. Obtain a power supply with a greater current output. With a higher output, the optimum current density could be determined in relation to rate of dissolution and the temperature of the electrolyte.
5. Determine how much heel is left; i.e., how much plutonium is dissolved before the metallic plutonium falls off the tantalum anode rod. If the heel is excessive, a different method for attaching the plutonium to the tantalum anode should be devised.
6. Investigate the long-term corrosion problems that might arise from the oxides of nitrogen that are produced.
7. Investigate the mechanism of dissolution. From available information, it would appear that the "electrolytic" part of the dissolution is of minor significance compared with the apparent "chemical" part.
8. Investigate the use of alternating rather than direct current. Since electrolysis apparently is not the principle mode of dissolution, alternating current might be just as efficient as direct current, and it probably would be less expensive.

An electrolytic dissolution procedure for plutonium appears to have a significant advantage over the

sulfamic acid dissolution procedure now being used. This advantage lies in the fact that no explosive residue is produced.

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