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ANION EXCHANGE RECOVERY OF
PLUTONIUM FROM REDUCTION RESIDUES

by

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ABSTRACT

An anion exchange process was demonstrated for the recovery of plutonium from waste produced in the reduction of plutonium salts to the metal. Plutonium in a highly salted 6M nitric acid solution derived from the dissolution of slag and crucible waste was separated from impurities by absorbing the Pu(IV) nitrate complex on the anion exchange resin and subsequently eluting with dilute nitric acid. A flowsheet for plant operation is presented.

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ANION EXCHANGE RECOVERY OF PLUTONIUM FROM REDUCTION RESIDUES

INTRODUCTION

When plutonium tetrafluoride is reduced to the metal by reaction with calcium⁽¹⁾, unreacted plutonium compounds and fragments of the metal remain in the reduction residue. The quantity of plutonium present is sufficient to require recovery from the residues, which consist of the slag, sand, and crucible. The principal constituents of the slag are calcium fluoride and calcium iodide; magnesium oxide is the principal constituent of the sand and crucible. These materials may be partially dissolved in nitric acid and, after removal of solids by filtration, a solution of plutonium in nitric acid is available for further processing. In addition to plutonium the solution contains macro amounts of aluminum, calcium, magnesium, and fluoride.

The absorption of the Pu(IV) nitrate complex by anion exchange resins has been studied by Aiken⁽²⁾ and by Ryan and Wheelwright⁽³⁾. These studies showed that plutonium was absorbed efficiently from solutions 7-8 molar in nitric acid. Preliminary studies showed that plutonium was absorbed from a nitric acid solution that contained aluminum, calcium, and magnesium. Thus, it appeared that an anion exchange process could be devised for recovering and purifying the plutonium contained in reduction residues. The laboratory work reported here was designed to demonstrate the feasibility of the process and to develop a flowsheet for tests in plant equipment.

SUMMARY

In laboratory tests plutonium was recovered by anion exchange from solutions that simulated the wastes produced in the reduction of plutonium fluoride to the metal. The product solution was satisfactory for subsequent processing by peroxide precipitation; the concentration of plutonium was about 45 g/l, and metallic impurities were present in concentrations less than 400 parts per million parts of plutonium. A flowsheet for plant operation was tested successfully. The time cycle for this flowsheet was about seven hours, and the loss of plutonium to waste was 0.4%.

The nitric acid solution derived from dissolution of the slag, sand, and crucible waste was fed to a column loaded with "Dowex" 21K, 50-100 mesh, anion resin. After the column was washed with 8M nitric acid - 0.002M sulfamic acid, it was eluted with 0.3M nitric acid. Both absorption and elution were carried out successfully at 45°C.

DISCUSSION

When the slag, sand, crucible fragments, and small amount of plutonium in the reduction residues are digested with nitric acid, most of the solids are dissolved. Nitrite is added in the digestion step to assist in the removal of iodine that is present in the slag as calcium iodide. After the iodine is completely volatilized from the solution, the insoluble residue is filtered off and the filtrate containing the plutonium has the following approximate composition.

Approximate Composition
of Slag and Crucible Dissolver Solution

<u>Constituent</u>	<u>Conc, M</u>	<u>Constituent</u>	<u>Conc, M</u>
H ⁺	6	Mg	1.3
NO ₃ ⁻	10	Al ^(a)	0.3
F ⁻	0.2	Ca	0.2
Fe, Co, Ni	0.01	Pu(IV)	0.004

(a) Aluminum is added to the solution to reduce corrosion of process equipment by the fluoride ion.

In preliminary experiments the equilibrium distribution coefficient of plutonium in the dissolver solution was measured. The absorption of plutonium in column operation was then studied and the effects of variables were determined in the absorption, washing, and elution steps. Finally, a flowsheet for plant operation was designed and tested.

EQUILIBRIUM ABSORPTION OF PLUTONIUM FROM SLAG AND CRUCIBLE SOLUTION

The absorption of plutonium was studied from synthetic slag and crucible dissolver solution prepared from the appropriate reagents. To simulate the digestion of the residues with nitric acid, the solution was heated for several hours in the presence of nitrite. In all experiments plutonium was present in the (IV) state after the heating step so that no adjustment of the valence state was required.

The equilibrium distribution coefficient, K_d , of plutonium from the synthetic dissolver solution was measured under different conditions. Data in the following table show that the absorption was not affected as the acid was varied from 5.5 to 6.5M. The presence of fluoride in the solution decreased the distribution coefficient; however, absorption was satisfactory at concentrations of fluoride up to 0.8M.

Equilibrium Absorption of Pu from
Slag and Crucible Dissolver Solution

Resin: "Dowex" 1-X4 (50-100 mesh)
 Solution: Synthetic slag and crucible solution
 Contact time: 48 hours, 1 ml resin/100 ml solution

<u>Acid Conc, M</u>	<u>Fluoride Conc, M</u>	<u>K_d</u>
5.4	0.2	1128
6.5	0.2	1215
6.5	0	816
6.5	0.4	634
6.5	0.8	555

COLUMN OPERATION

ABSORPTION OF PLUTONIUM

The capacity of the resin as determined under the nonequilibrium conditions of column operation is dependent on the flow rate and the plutonium concentration of the feed solution. The influence of these variables on the absorption of plutonium in a column operation is shown in the following table and in Figure 1.

Capacity of Resin as a Function
of Plutonium Concentration in the Feed

Feed: Synthetic slag and crucible solution
 Resin: "Dowex" 1-X8 (50-100 mesh)
 Column: 0.36 cm x 35.6 cm depth
 Flow rate: 4.2 ml/(min)(cm²)
 Column operated
 to 10% breakthrough: $C/C_0 = 0.1$
 Temperature: 24°C

<u>Pu Conc in Feed, g/l</u>	<u>Bed Volumes of Feed</u>	<u>Pu Absorbed, mg/ml resin</u>
0.75	52.8	37.4
1.37	23.7	30.8
1.95	14.9	27.6
3.85	5.2	19.0

Data in the table show that at a constant volumetric flow the capacity of the resin is much higher for the more dilute feed solutions. From the data in Figure 1 it is seen that flow rates below 10 ml/(min)(cm²) give low losses in processing large volumes of feed. In plant operation these data may be used to establish time cycles and to select the proper operating conditions for a given feed solution.

FIGURE 1 - EFFECT OF FEED FLOW RATE ON THE ABSORPTION OF PLUTONIUM FROM SYNTHETIC SLAG AND CRUCIBLE SOLUTIONS

The capacities of three different resins were measured in column operation with the results as shown below. The equilibrium exchange capacity of "Dowex" 1-X8 per unit volume is 20% greater than that of the lower cross-linked "Dowex" 1-X4. However, in nonequilibrium column operation the higher diffusion rate in the more porous "Dowex" 1-X4 resin permitted it to attain a higher capacity for a given contact time. "Dowex" 21K was selected for plant operation because of its higher capacity in column operation.

Capacity of Different Resins in Column Operation

Feed: Synthetic slag and crucible solution (Pu = 1.0 g/l)
Column: 0.40 cm x 35.6 cm depth
Flow rate: 10 ml/(min)(cm²)
Temperature: 45°C

<u>Resin</u>	<u>Pu Absorbed, mg/ml resin</u>
"Dowex" 21K	60
"Dowex" 1-X4	54
"Dowex" 1-X8	42

Ryan and Wheelwright⁽³⁾ state that the maximum absorption of the plutonium nitrate complex by the anion resin is obtained at approximately 65°C from a 7.2M nitric acid solution. The plutonium contained in the slag and crucible solution was also absorbed more completely at 65°C; however, the solution attacked the resin at this elevated temperature causing both "Dowex" 1-X4 and 21K to swell considerably and partially dissolve. Satisfactory absorption was obtained at the lower temperature of 45°C with no apparent damage to the resin. No change in capacity was observed for "Dowex" 21K resin after several weeks use in column tests at 45°C.

SEPARATION OF PLUTONIUM FROM IMPURITIES

After absorption of plutonium from the feed solution, the resin was washed with 8M nitric acid containing 0.002M sulfamic acid to improve the separation of plutonium from impurities. In the experiments with the washing procedure the volume of wash was held in the range of 1-2 bed volumes and the flow rate was held at 6 ml/(min)(cm²). The results showed that there was very little improvement in the removal of impurities when the wash was increased above this range.

Sulfate ion, which may be present at times in low concentrations, did not interfere with the absorption of plutonium from the slag and crucible solution. Although sulfate is more strongly absorbed by the anion resin than is the nitrate ion, the high concentration of nitrate (9.5M) reduces the absorption of sulfate to a negligible level. The product solution from a feed that was 0.15M in sulfate contained less than 9×10^{-5} M sulfate after a single cycle of anion exchange.

Excellent separation of plutonium from cations other than aluminum was achieved in a single cycle of anion exchange. Magnesium, calcium, chromium, nickel, and iron in the product were less than 200, 200, 2, 20, and 0.2 parts per million parts of plutonium, respectively. Aluminum in the product was about 400 parts per million parts of

plutonium. Attempts to reduce the aluminum in the product by adding small amounts of fluoride to the 8M nitric acid wash resulted in excessive losses of plutonium. A more detailed study of the washing procedure was not made since the purity of the product was adequate for subsequent processing.

ELUTION OF PLUTONIUM

Plutonium may be eluted from the resin either by reducing Pu(IV) to Pu(III) or by decomposing the Pu(IV) nitrate complex with dilute nitric acid. Ryan and Wheelwright⁽³⁾ determined the maximum product concentration obtainable at various nitric acid concentrations. In the reduction procedure 0.1M ascorbic acid in 0.5M ammonium nitrate was used as the elutriant. This procedure required that the 8M nitric acid wash be completely displaced with a salt solution such as ammonium nitrate to prevent decomposition of the reductant by the strong acid. The preliminary investigations showed that plutonium could be eluted in the trivalent state to give a concentration of about 35 g/l in the product solution. Where the dilute nitric acid elutriant was used at elevated temperatures, 45-55°C, the plutonium nitrate was eluted at an average concentration of 50 g/l. Figure 2 shows typical elution curves for plutonium and acid at room temperature with 0.35M nitric acid as the elutriant. These data show that elution with dilute acid at elevated temperature provides the maximum concentration of plutonium in the product and a shorter time cycle. Since a high concentration of plutonium is advantageous for subsequent processing, this elution procedure was selected for the plant flowsheet.

FIGURE 2 - CONCENTRATIONS OF PLUTONIUM AND H⁺ DURING ELUTION STEP

PLUTONIUM RECOVERY FLOWSHEET

RECOVERY TESTS

Two series of runs were made on synthetic slag and crucible dissolver solutions containing approximately 1 g/l of plutonium. The operating sequence in both series was the same as that shown in Figure 3.

OPERATING SEQUENCE

Recondition Wash
Feed (1) 5 minutes, wash effluent to Feed Tank for recycle

Absorption
Feed (2), 4.3 hours - Feed effluent to waste

Decontamination Wash
Feed (3), 5 minutes - Wash effluent to waste

Elution
Feed (4), 2.7 hour - Displacement cut (4A) to Feed Tank for Recycle
Product cut (4B) to product tank

Recycle
The recycle solution is blended with the feed for the next column operation.

FLOW RATES

(1), (2), and (3) 10 ml/(min)(cm²)
(4) 0.5 ml/(min)(cm²)

FIGURE 3 - PLUTONIUM ANION EXCHANGE RECOVERY FLOWSHEET - PLANT SCALE

In the first series of three runs, the plutonium was recovered at an average concentration of 47 g/l and the average loss was 0.4%.

Recovery Tests

Column: 0.36 cm x 35.6 cm depth
 Resin: "Dowex" 1-X4 (50-100 mesh)
 Feed: 1.0 g Pu/l, 12 ml/(min)(cm²) upflow
 Decontamination wash: 100 ml 8M HNO₃ - 0.002M ferrous sulfamate, 6 ml/(min)(cm²) flow rate
 Elutriant: 0.3M HNO₃, 0.5 ml/(min)(cm²) downflow
 Temperature: Feed and elutriant, 55 ± 5°C
 Plant scale: 1/650

<u>Vol. of Feed, liter</u>	<u>Pu in Waste, mg/l</u>	<u>Pu Conc. in Product Cut, g/l</u>	<u>Total Pu in Product Cut, %</u>	<u>Total Pu in Recycle, %</u>
1	0.8	48	96	4
1	2.1	46.9	95	5
1	5.1	45.2	94	6

In the second series of three runs the flowsheet shown in Figure 3 was tested at 1/49 plant scale. The operating conditions and a summary of the data are given in the following table.

Recovery Tests

Column: 2.54 cm x 35.6 cm depth
 Resin: "Dowex" 21K (50-100 mesh)
 Feed: 1.13 g Pu/l, 12 ml/(min)(cm²) upflow
 Decontamination wash: 200 ml 8M HNO₃ - 0.002M ferrous sulfamate, 6 ml/(min)(cm²) flow rate
 Elutriant: 0.3M HNO₃, 1 ml/(min)(cm²) downflow
 Temperature: Feed and elutriant, 45°C
 Plant scale: 1/49

<u>Vol. of Feed, liter</u>	<u>Pu in Waste, mg/l</u>	<u>Pu Conc. in Product Cut, g/l</u>	<u>Total Pu in Product Cut, %</u>	<u>Total Pu in Recycle, %</u>
7.2	1.8	38	94	6
8.0	1.9	36	96	4
8.0	2.2	45	97	3

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For this series the average concentration of plutonium in the product was 42 g/l, and the average loss was about 0.4%. These tests show that the anion exchange process is satisfactory for plant operation.

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