HANFORD NEPTUNIUM OXALATE-OXIDE PROCESS EXPERIENCE

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Photostat Price \$ 3.30

Microfilm Price \$ 2.40

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

Process Chemistry
Research and Engineering
Chemical Processing Department

July 1, 1959

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Operated for the Atomic Energy Commission by
General Electric Company under Contract #AT(45-1)-1350

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INTRODUCTION

In recent months, relatively large quantities of neptunium-237 have been recovered from Hanford irradiated uranium. The over-all recovery process consisted of 1) isolation from Purex plant solutions by solvent extraction, to yield an impure neptunium nitrate solution contaminated principally with uranium, plutonium, and fission products⁽¹⁾; 2) purification by anion exchange⁽²⁾; 3) precipitation of neptunium(IV) oxalate; and 4) calcination of the oxalate to yield neptunium(IV) oxide, NpO_2 . This paper describes the oxalate precipitation process investigations and results.

SUMMARY AND CONCLUSIONS

A satisfactory neptunium oxalate process has been developed for the final purification of Hanford anion exchange product and its conversion to neptunium(IV) oxide. In the process which appears best adapted for routine operation, neptunium(IV) oxalate was precipitated by the direct addition of the anion exchange product, containing 15-20 grams/liter neptunium nitrate solution [$> 99\%$ neptunium(IV)] to an oxalic acid-nitric acid mixture. The reagent volumes and concentrations were adjusted to give a final slurry of about 0.1M oxalic acid and about 2.0 M nitric acid. After filtration, the precipitate, apparently $\text{Np}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ was washed with dilute nitric acid and converted to NpO_2 by igniting in air at 550-600 C. The filtrate was concentrated by thermal evaporation to "kill" oxalic acid and hydrazine, and returned to anion exchange for neptunium recovery. This process yielded a neptunium oxide which assayed 99.7% NpO_2 with a total metallic impurity content of less than 500 ppm of neptunium. Filtrate neptunium concentration averaged about 50 milligrams per liter, which represented a recycle value of 0.25% of throughput.

The processing rate was limited by the digestion time required to obtain a filterable precipitate. The fine, grayish-white precipitate formed initially was very difficult to filter. This material gradually changed to a brilliant green, readily-filterable precipitate when left in contact with the mother liquor. The rate of formation of the green crystalline precipitate appeared to be more characteristic of the particular batch of anion exchange product than a property of precipitation conditions. A definite correlation was established between the rate of formation of the filterable material and the temperature of the slurry, the rate increasing with increasing temperature. However, the rate did not appear to be materially affected by the speed or order of chemical addition or by the nitric acid concentration and/or the neptunium concentration of the slurry.

The oxalate process achieved little or no separation from plutonium or from the neptunium-237 daughter, protactinium-233.

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DISCUSSION

Early Experience

A simple process was needed to convert Hanford neptunium anion exchange product, a dilute neptunium nitrate solution, to neptunium oxide. Since additional purification beyond that achieved by the anion exchange step was felt desirable, a precipitation process was chosen for part of the final conversion step rather than direct calcination of the nitrate.

The choice of the oxalate precipitation for purification was based largely on the fact that a plutonium oxalate process had been used successfully at Hanford for years. As a result, the precipitation conditions studies first were patterned after the standard plutonium oxalate process, which used a concentrated plutonium nitrate feed and a pre-reduction step prior to the oxalate precipitation step.

The flow diagram for the similar neptunium oxalate process is shown in Figure 1. As is shown in the diagram, dilute neptunium(IV) nitrate solution was concentrated by thermal evaporation to yield a concentrated solution containing 150-200 g/l Np and about 8-10 M HNO_3 . After concentration, the solution was allowed to cool to about 50-70°C, and reduction of the neptunium [now neptunium(VI); due to oxidation by nitric acid during concentration] was achieved by the addition of an equal volume of an aqueous semicarbazide solution to yield a feed solution containing about 75-100 g/l Np(IV), about 4-5 M HNO_3 , and about 30 g/l semicarbazide. This solution was then added to enough 1 M oxalic acid and water to precipitate the neptunium as the di-oxalate and give a mother liquor about 0.1 M in oxalic acid and 2.0-3.0 M in nitric acid. The slurry was agitated until a filterable precipitate was formed. After filtration, the precipitate was washed with dilute nitric acid, and ignited to NpO_2 in air at 550-600 C. The filtrate was concentrated by thermal evaporation, which concentrated the neptunium and "killed" the semicarbazide and oxalic acid, and was returned to the anion exchange unit for neptunium recovery.

Typical experimental results are given in Table I. As is shown by the data, the process yielded product of the desired purity, neptunium content, with, in general, low filtrate losses. The oxalate process as shown by the data did not, however, give any significant separation from plutonium or the neptunium-237 daughter - protactinium-233.

Initially, difficulty was encountered in consistently attaining complete precipitation of the neptunium. This was found to be due principally to the incomplete reduction of neptunium(V) to neptunium(IV) prior to precipitation. It was found that the reduction of neptunium(V) to neptunium(IV) with semicarbazide at room temperature was extremely slow⁽³⁾ in the absence of a catalyst and also that the rate was quite acid dependent, with the rate of reduction decreasing with decreasing acidity. Satisfactory reductions were obtained (complete in 30 minutes) with semicarbazide, using 0.6 grams of semicarbazide per gram of neptunium and 0.001 M ferrous ion as a catalyst,

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FIGURE 1

FLOW CHART: NEPTUNIUM OXALATE "CONCENTRATED STRIKE"

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TABLE I

NEPTUNIUM OXALATE "CONCENTRATED STRIKE" RESULTS

Run No.	% (1) NpO ₂	Product Quality			Average Filtrate Assay	
		TMI(2) PPM	Decontamination Factor Pu	Pu-233	Mg/liter Np-237	Per Cent Throughput
1	99.8	800	1	1	38	0.06
2	99.7	600	1	1	29	0.05
3	99.8	400	1	1	27	0.04
4	99.6	300	1	1	16	0.04

- (1) Neptunium assay by controlled potential coulometer
- (2) TMI, total metallic impurities, computed from the sum of individual spectrographic values for K, B, Ca, Cr, Fe, Cu, Mg, Mn, Na, Ni, Si, Cd, V, Mo, Be, As, and Zn.

when the nitric acid was maintained between 4.0 - 5.0 M and the temperature of the reaction above 50 C. In addition, it was found that the rate of reduction with these reagents in the precipitation step (in the presence of oxalate ion) was quite slow. As a consequence, low filtrate values (10-20 mg/liter in neptunium), were obtained only when the neptunium was essentially all in the plus four oxidation state at the beginning of the precipitation step.

Since the original precipitation conditions, which aimed for an 0.1 M oxalic acid concentration and 2.0 - 3.0 M nitric acid concentration in the mother liquor, gave acceptable product purities and neptunium solubilities (filtrate values) near the reported⁽⁴⁾ equilibrium solubility, the effects of these variables were not studied extensively. However, it can be definitely stated that the close control of these variables, other than the need for the stoichiometric amount of oxalate, was not critical. Variation in the nitric acid concentration or excess oxalic acid concentration by as much as 50% from the original precipitation conditions did not appear to affect the results materially.

One of the problems of concern was that of obtaining a filterable oxalate precipitate. It was found that when neptunium(IV) nitrate solution is added to 1 M oxalic acid, a fine, light-gray slurry, which can be filtered only with difficulty, is formed. With time, however, this gray slurry gradually changes to a bright green, readily-filterable slurry.

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In an endeavor to find the optimum conditions for obtaining the desirable, green crystal form, a study was made on the effect of variation in the neptunium and nitric acid concentrations and the temperature of the slurry. The order and rate of reagent additions were also varied. Of these variables, only temperature was found to materially affect the rate of formation of the green crystalline material, with the rate at 50 C approximately double that at 25 C. However, it was observed that the rate of conversion of the gray to the green slurry also varied between batches of the ion exchange product used as starting material, or feed. When feed material eluted from old resin (resin in service for several runs) was used, the rate of green precipitate formation was about four times as fast as for material from new resin. Also of interest was the fact that under a given set of conditions the rate of greening was practically constant. When the initial light gray precipitate was left in contact with the mother liquor without agitation, the green precipitate could be observed as a slowly moving green layer, the color moving from the bottom of the settled precipitate to the top at a constant rate.

Although the original process gave satisfactory results from the standpoint of purity, it had several disadvantages. First was the need for the evaporation step. Secondly, the concentration step oxidized the neptunium(IV) in the anion exchange product to neptunium(VI), which necessitated a reduction step prior to precipitation. In addition, the use of a "concentrated strike" required the close control of concentration and volumes to maintain the proper oxalate and nitric acid balance.

As a result of these considerations, the "dilute strike" procedures described in succeeding sections was designed and tested.

"Dilute Strike" Process

The flow diagram for the "dilute strike" process is shown in Figure 2. As shown in the diagram, hydrazine was used as a holding reductant when the neptunium(IV) nitrate was eluted from the resin. The dilute feed was then precipitated by the direct addition of the feed to sufficient oxalic acid and nitric acid to precipitate the neptunium as the di-oxalate and give a mother liquor containing 0.1 M oxalic acid and about 2.0 - 3.0 M HNO_3 . The rest of the process is identical to the one previously described.

Process Results

Typical results obtained in studies of the "dilute strike" are given in Table II. As shown by the data, this process gave a product of somewhat higher purity than the "concentrated strike". As with the latter, the "dilute strike" gave little or no separation from plutonium or protactinium. Filtrate neptunium concentrations were higher by a factor of two than for the original process, with the total losses to recycle being considerably higher due to the volumes involved. This fact was of no real concern, since all of the material could be recycled to the anion exchange unit for recovery. The comparatively high neptunium filtrate concentrations were attributed to the presence of minor concentrations of neptunium(V) in the feed.

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FIGURE 2

NEPTUNIUM OXALATE "DILUTE STRIKE" PROCESS

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TABLE II

NEPTUNIUM OXALATE "DILUTE STRIKE" PROCESSING RESULTS

Run No.	Product Quality		Decontamination Factor		Average Filtrate Assay	
	% (1) NpO ₂	TMI (2) ppm	Pu	Pa-233	Mg/liter Np-237	% Thru-put
1	99.8	290	~1	~1	12	0.06
2	99.8	400	~1	~1	41	0.21
3	99.4	220	~1	~1	62	0.31
4	99.8	300	~1	~1	76	0.38

- (1) Neptunium assay by controlled potential coulometer.
- (2) TMI, total metallic impurities computed from the sum of individual spectrographic values for K, B, Ca, Cr, Fe, Cu, Mg, Mn, Na, Ni, Si, Cd, V, Mo, Be, As, and Zn.

TABLE III

SEPARATION OBTAINED FROM METALLIC IMPURITIES
BY THE "DILUTE STRIKE" PROCESS

Metallic Impurity	Average Metallic Impurity Concentration PPM ⁽¹⁾		
	Feed Nitrate Solution	Np Oxide Product	Approximate Separation Factor
Aluminum	500	10	50
Calcium	10,000	150	67
Chromium	20	< 2	> 10
Copper	10	< 5	> 2
Iron	3,000	< 10	> 300
Magnesium	1,000	10	100
Manganese	200	3	67
Nickel	100	4	25
Sodium	200	15	13
Silicon	200	2	100
Zinc	1,000	< 100	> 10

- (1) Impurities determined by spectrographic analysis and reported in parts per million parts of neptunium.

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Metallic impurities in the product and the separation obtained from these impurities by the "dilute strike" procedure are shown in Table III. As the data shows, good separation was obtained from the principal feed impurities, iron, calcium, aluminum, and magnesium. The data, although not as positive for the trace impurities, indicates that good separation could be obtained from chromium, nickel, sodium, and zinc.

Process Equipment

The test equipment consisted of: 1) a Pyrex concentrator; 2) a Pyrex precipitation pot equipped with a mechanical agitator, an air sparging system, and a stainless steel discharge valve; 3) a 3-1/4-inch diameter, coarse porosity, fritted glass filter (Corning catalog No. 36060); a 5-inch "Hoskins" #104 pot furnace; and 4) a Pyrex ignition beaker.

The "Hoskins" furnace was modified to accommodate the glass filter so that the filter could also serve as the crucible. However, filter breakage in the muffle was excessive with an average life of two calcinations per glass filter. As a consequence, a shortened 600 ml Pyrex beaker was substituted as a crucible. Because of this, the ignition temperature was kept below 600 C to prevent softening of the Pyrex beaker. All product data shown in Tables I, II, and III were obtained using the Pyrex beaker.

Solutions were transferred to and from the anion exchange cell and hood by pump or vacuum through 1/4-inch stainless steel lines housed in 3/8-inch stainless steel jackets. Feed addition was made pumping the anion exchange product into the precipitation pot on top of the nitric acid-oxalic acid solution. The slurry was agitated with a mechanical stirrer and discharged by gravity through the discharge valve, air sparging to dislodge sediment. Filtration was aided by vacuum. Under vacuum, a 200-400 ml per minute filtration rate was attained for the coarse, green precipitate with the sintered glass filter.

Filtrate Treatment

The filtrate was concentrated by thermal evaporation to "kill" oxalate and hydrazine before return to the anion exchange unit for neptunium recovery. The evaporative "kill" technique was quite similar to the one described by Berglund (5) with the exception that the filtrate was concentrated to about 8-10 M nitric acid to insure a complete "kill" rather than boiling for a fixed time period. When a more rapid filtrate treatment was needed, a permanganate "kill" followed by the addition of ferrous ion (to dissolve MnO_2) was used.

Analytical

The neptunium feed was assayed by direct alpha counting and by X-ray absorption. The filtrate was assayed for neptunium-237 by the conventional TTA-extraction-total alpha counting method, using a neptunium-237 specific activity of 5.78×10^9 d/m/g. The final product oxide was assayed by dissolving a weighed amount of the oxide in hot nitric acid and measuring the

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dissolved neptunium by the controlled potential coulometric method of Stromatt (6).

Oxalate ion in the filtrate was determined with permanganate after the hydrazine had been destroyed with nitrite. Nitrite was added to destroy hydrazine and the excess nitrite was destroyed with sulfamic acid.

Protactinium-233 was determined with a gamma spectrometer and was usually reported as per cent to equilibrium of the daughter in the Np-237-Pa-233 parent daughter relationship.

Plutonium in the product and feed was determined by alpha energy analysis.

Composition of the Oxalate Precipitate

The composition of the dry oxalate precipitate was presumed to be $\text{Np}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$. The fact that the precipitate has two oxalates per neptunium was verified by making material balances for neptunium and oxalate on the precipitation cycle. However, the water of hydration was only checked approximately. The direct ignition of the wet (partially air dried) precipitate showed an apparent molecular weight of 532 which corresponds to $\text{Np}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ with some surface moisture.

Radiation and Criticality Control

The principal danger from the standpoint of a nuclear incident with the test process equipment was that of receiving critical amounts of plutonium rather than neptunium-237. As a safeguard against this occurrence, a total alpha measurement was made on each batch of feed. The principal control for the neptunium-237 in this regard was the use of a 500 gram limit for the total amount present in any single configuration having a spherical radius of less than three feet. The 500-gram limit (7) is believed to be a highly conservative figure.

Radiation exposure was a problem only during the oxide handling step. After calcination, the powder was transferred to 8 ounce plastic bottles and weighed to fixed amounts. When the powder was an appreciable way (>15%) to equilibrium in the protactinium daughter, hand exposures during the weighing procedure ranged from 500-1000 millirads/hour. After weighing, the powder was packaged in 1/8-inch thick lead cylinders (about 100-150 grams NpO_2 per cylinder) and with this amount of shielding could be handled without difficulty.

Need for Further Work

As yet, the nature of the two precipitates - the initial grayish-white, unfilterable precipitate and the green, crystalline material - has not been ascertained. A knowledge of the difference in the nature of the two and a positive means of controlling the rate of formation of the green, filterable

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material is needed. Separation factors for the various fission products are also needed for determining the application of the oxalate process to other feed solutions.

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