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PRECIPITATION OF NEPTUNIUM OXALATE AND CALCINATION TO NEPTUNIUM OXIDE

[redacted]

by

J. A. Porter

Separations Chemistry Division

July 1961

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PRECIPITATION OF NEPTUNIUM OXALATE AND CALCINATION TO NEPTUNIUM OXIDE

[redacted]

by

J. A. Porter

Work done by

J. A. Porter and E. K. Dukes

July 1961

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ABSTRACT

Two procedures were developed for the quantitative precipitation of neptunium(IV) oxalate that filters rapidly and is readily calcined to the oxide. In the preferred procedure the oxalate was precipitated at elevated temperature from solutions of low acidity. In the alternative procedure the oxalate was precipitated at room temperature from solutions of higher acidity. Neptunium oxide was prepared by calcining the oxalate at 500°C in a flowing stream of air or nitrogen.

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PRECIPITATION OF NEPTUNIUM OXALATE AND CALCINATION TO NEPTUNIUM OXIDE

INTRODUCTION

A process was required for the preparation of neptunium oxide from moderately concentrated solutions of neptunium in nitric acid. The process was to be applied to the isolation of neptunium from the end streams of a variety of radiochemical separations processes, including ion exchange and solvent extraction systems. Two routes to the oxide were considered - precipitation of neptunium(IV) oxalate or neptunium(IV) peroxide and subsequent calcination of either compound to neptunium oxide. The oxalate precipitation was selected in preference to the peroxide because of shorter filtration times, lower solubility and hence less loss of neptunium, less sensitivity to operating variables, and greater potential for decontaminating the neptunium from impurities, especially residual fission products.

This report summarizes the laboratory development of procedures for the efficient precipitation of neptunium(IV) oxalate from nitric acid solutions and for the calcination of the oxalate to the oxide. It also describes the successful application of the procedures in pilot-scale operations. Studies of the neptunium(IV) peroxide precipitation are reported in a separate document(1).

Concurrently with the present work, a process was developed at Hanford(2) for the preparation of neptunium(IV) oxalate and neptunium oxide. The Hanford procedure yields a neptunium(IV) oxalate precipitate that must be digested for extended periods before filtration, and losses of neptunium to the filtrate are greater than with the procedures reported here.

SUMMARY

Two acceptable procedures were developed for the precipitation of neptunium(IV) oxalate that filters rapidly and is readily calcined to the oxide. In the preferred precipitation procedure, Np(IV) is precipitated by the addition of oxalic acid solution to a feed solution containing about 5 to more than 50 grams of neptunium per liter in 1 to 4M nitric acid at 50°C. The neptunium feed solution contains 0.05M hydrazine to stabilize the Np(IV) valence state, and ascorbic acid is added before precipitation to reduce any Np(V) to Np(IV). The presence of Np(V) results in higher losses of neptunium to the filtrate.

In the alternative procedure, which allows precipitation at room temperature, the conditions are the same with the exception that the nitric acid concentration must be adjusted to about 4M or above. The higher acidity accelerates the rate of reduction of Np(V) by ascorbic acid, and thus compensates for the lower temperature. Filtrate losses

[redacted] [redacted]

of neptunium are less than 10 milligrams per liter with either procedure and, within rather wide limits, both procedures are generally insensitive to process variables. Essentially no separation of neptunium from plutonium or protactinium is achieved by the oxalate precipitation, but significant separation from zirconium-niobium and ruthenium is obtained.

Air-dried neptunium(IV) oxalate was shown to have the composition $Np(C_2O_4)_2 \cdot 6H_2O$. This compound was dehydrated and decomposed to NpO_2 by heating it to 500°C under a flowing stream of air or nitrogen. The oxide was dark olive in color, was free flowing, and had an average bulk density of 2.5 grams per cubic centimeter. The purity of the oxide was variable, being dependent on the purity of the feed solution.

The precipitation, filtration, and calcination of the oxalate were demonstrated to be reliable and effective for process use by applying them in about 100 runs on a scale of 50 grams of neptunium.

DISCUSSION

EXPERIMENTAL METHODS

LABORATORY TESTS

Pure solutions of Np(IV) in dilute nitric acid required for precipitation studies were prepared by anion exchange from a stock of purified neptunium. Solutions of Np(V) used in screening tests for reductants and in rate studies were prepared by heating anion exchange eluate containing Np(IV) to 55°C for 30 minutes and allowing it to stand at room temperature for 3 days. Examination of these Np(V) solutions with a Carey recording spectrophotometer showed the Np(IV) plus Np(VI) content to be less than 3%; solvent extraction tests showed the Np(IV) content to be less than 0.3%.

Neptunium analyses were performed by standard alpha counting techniques and by controlled potential coulometry. Solutions that also contained Pu^{238} were processed through 3 thenoyltrifluoroacetone (TTA) extraction cycles to separate the neptunium and plutonium before the fractions were analyzed by alpha counting and alpha pulse height analysis. Neptunium oxalate and neptunium oxide were dissolved in nitric acid and nitric acid - hydrofluoric acid solutions, respectively, to facilitate analyses. Fission product analyses were performed with a 256-channel gamma spectrometer and a gamma scintillation counter. Other metallic impurities were analyzed by emission spectroscopy.

In screening potential reagents for the reduction of Np(V) to Np(IV), pure concentrated solutions of Np(V) were diluted with nitric acid to give test solutions of 1.2 g/l of neptunium and the desired acidity. The desired concentration of reductant was then added, and the reaction was allowed to proceed for a designated period. The reaction was quenched by a 10^3 dilution with 1M nitric acid, and the extent of reduction was determined immediately. In tests at elevated temperatures, the reductant was added after the test solution was heated to the desired temperature, and the reaction was quenched by rapid cooling and dilution. The extent of reduction was determined by analyzing the quenched reaction mixture for Np(IV). An aliquot of the reaction mixture was contacted with an equal volume of 10% TTA in xylene to extract the Np(IV) produced by the reduction. Alpha counting of an aliquot of the organic phase permitted calculation of the per cent reduction. The TTA extraction procedure gives essentially complete extraction of Np(IV) to the exclusion of Np(V); a portion of any Np(VI) present is also extracted. The error introduced in these tests by the extraction of Np(VI) was not significant because of the low Np(VI) concentration and because most of the test reductants were capable of reducing Np(VI) to Np(V) even if further reduction did not occur.

The equilibrium solubility of neptunium oxalate in nitric acid - oxalic acid solutions at room temperature was determined by two procedures. In the first procedure, neptunium oxalate was precipitated with various excesses of oxalic acid from Np(IV) solutions containing various concentrations of nitric acid. After equilibration, the solutions were analyzed to determine the solubility of neptunium oxalate. In the other procedure, pure neptunium oxalate was equilibrated with various nitric acid - oxalic acid solutions, and the solubility was determined at equilibrium.

The filtration characteristics of neptunium oxalate slurries prepared by precipitation were evaluated in terms of the relative filtration factor. This factor is defined as the ratio of the time required to filter the slurry to the time required to filter an equal volume of water through the same filter under the same conditions.

PILOT-SCALE TESTS

The operability of the neptunium oxalate - oxide process was demonstrated in a pilot-scale facility. The equipment included a precipitator, a filter, associated tanks, and a calcination furnace. All equipment was constructed of type 304L stainless steel or materials of equivalent corrosion resistance. The precipitator was 6 inches in diameter, was fully baffled, and was equipped with a 3-inch-diameter, flat-bladed impeller, which was driven by a variable-speed air motor. Immersion-type heaters and an annular cooling water jacket were incorporated into the unit. The sides and bottom of the precipitator were insulated to facilitate temperature control. A maximum of 3.5 liters of feed solution containing about 100 grams of neptunium could be processed in the precipitator. The filter consisted of a housing and a removable filter boat. A 3-inch-diameter stainless steel frit welded into the bottom of the boat served as the filter medium. The mean pore size of the frit was 5 microns; the volume of the boat was about 500 cubic centimeters. A tube-type furnace was used for calcining the neptunium oxalate to the oxide. The furnace tube, which was 3 inches in diameter and 12 inches long, accommodated a 250-cubic-centimeter boat and could be swept with air or nitrogen. All process equipment was located within a containment facility.

Neptunium feed solutions for the pilot-scale tests were prepared from irradiated Np^{237} oxide target elements. As described elsewhere(3), the irradiated target elements were dissolved and processed by ion exchange to remove fission products, to isolate the Pu^{238} product, and to recover the unconverted Np^{237}. The process normally yielded a neptunium solution containing 30 to 35 g/l of Np(IV), stabilized by hydrazine, and having about 1M nitric acid. Low concentrations of Pu^{238}, fission products, and other metallic impurities were usually present in the final neptunium solutions.

DEVELOPMENT OF OXALATE PRECIPITATION PROCESS

It was desired that the process developed for the precipitation of neptunium oxalate be applicable to the isolation of neptunium from the end streams of various radiochemical processes. Although the radiochemical processes may differ markedly, it was anticipated that a final anion exchange concentration step for neptunium would be common to all. Therefore, procedures were developed for the precipitation of neptunium oxalate from feed solutions prepared by anion exchange. Such solutions normally contain about 1M nitric acid and variable concentrations of neptunium as Np(IV). The attainment of low neptunium losses in the oxalate precipitation is dependent upon all of the neptunium being in the Np(IV) state because the oxalate complexes of neptunium in other valence states are soluble.

SOLUBILITY MEASUREMENTS

The solubility of neptunium oxalate at room temperature as a function of nitric acid and oxalic acid concentrations was determined to establish the minimum neptunium loss attainable in the precipitation and to define the conditions for minimum loss. Solubility data obtained by the equilibration of pure neptunium oxalate with nitric acid - oxalic acid solutions are shown in Figures 1 and 2. Slightly higher solubilities were obtained when the oxalate was precipitated from solution and allowed to attain equilibrium. A stabilizing agent for Np(IV) was not present in the test solutions; the higher solubilities obtained by the precipitation technique were apparently due to the presence of traces of Np(V) in the feed solutions. The data show that the solubility of neptunium oxalate is rather insensitive to the concentrations of nitric acid and oxalic acid. At an

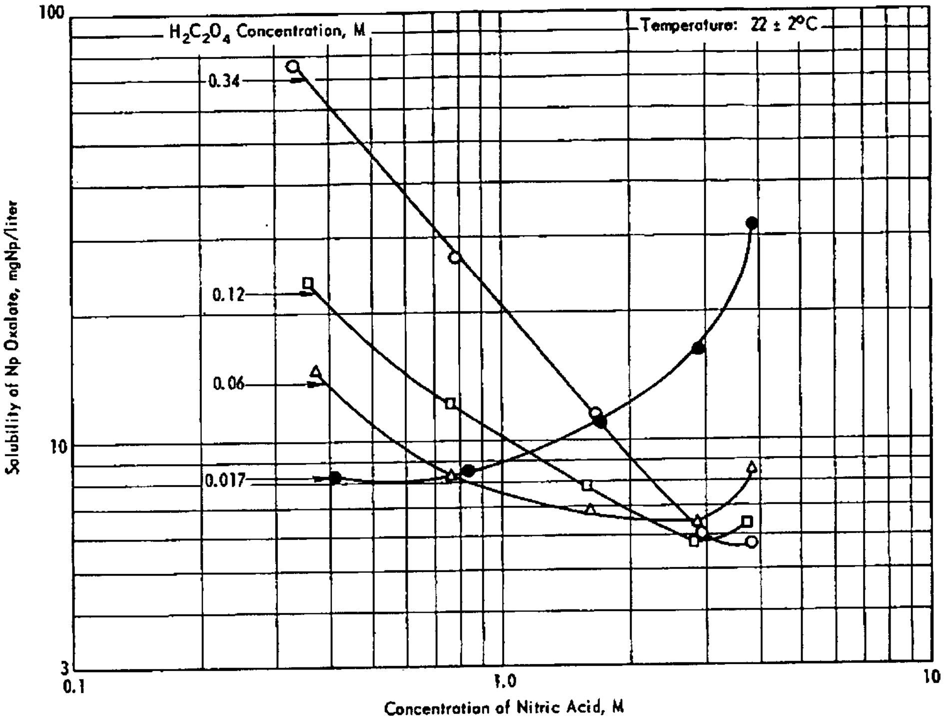

FIG. 1 THE EFFECT OF NITRIC ACID CONCENTRATION ON THE SOLUBILITY OF NEPTUNIUM OXALATE

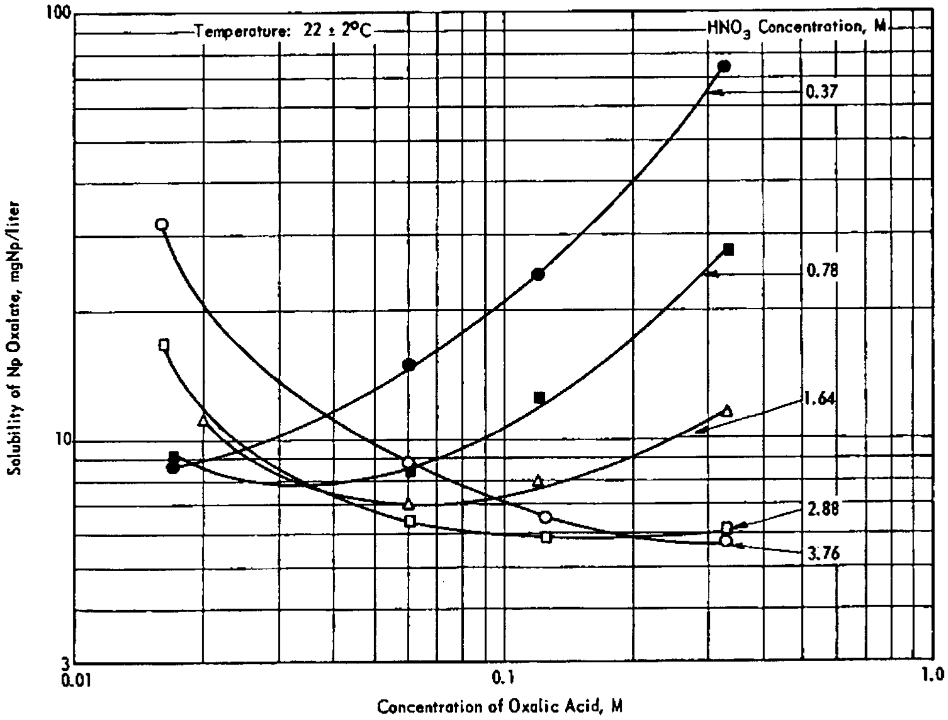

FIG. 2 THE EFFECT OF OXALIC ACID CONCENTRATION ON THE SOLUBILITY OF NEPTUNIUM OXALATE

oxalic acid concentration of 0.1M, the solubility varies only between 6 and 10 mg/l of neptunium as the nitric acid concentration is varied between 1 and 4M.

The data indicate that the solubility of neptunium oxalate in nitric acid - oxalic acid solutions is controlled by equilibria between neptunium oxalate complexes of varying solubility. Four oxalate complexes of Np(IV) have been reported(4). Minimum solubility apparently results when the free oxalate concentration is such that formation of the highly insoluble di-oxalate complex is favored. Increased solubility may result from formation of more soluble oxalate complexes (either higher or lower complexes) as the free oxalate concentration is varied from optimum values.

SCOUTING TESTS

Neptunium oxalate was precipitated in filterable form and with low losses in preliminary tests with about 100 mg of purified neptunium. The initial Np(IV) feed solutions were prepared by anion exchange and contained about 8 g/l of neptunium and about 1M nitric acid. The precipitations were performed at room temperature by slowly adding to the agitated neptunium feed solution a volume of 1M oxalic acid sufficient to complex all of the neptunium and to establish a 0.1M excess of oxalic acid in the final slurry. The slurry was digested for 30 minutes at 80°C to improve the filtration characteristics. High losses of neptunium to the filtrates were encountered when the precipitations were not performed immediately after feed preparation because of the instability of Np(IV) toward oxidation in nitric acid solution. It was found that a 0.05M concentration of hydrazine in the feed, introduced during the anion exchange elution step, would stabilize Np(IV) for a period of at least several days. Neptunium losses in precipitations with such stabilized feeds were 0.1 to 0.2%. The addition of ferrous sulfamate reductant to the feed solution immediately prior to precipitation reduced filtrate losses of neptunium to less than 0.1%, but the precipitate was highly contaminated with iron.

Precipitations with 0.5 g of neptunium at feed concentrations of 40 to 50 g/l substantiated the previous findings. In addition, hydroxylamine was found to be as satisfactory as hydrazine for stabilizing Np(IV) in nitric acid feed solutions for a period of at least 3 days. Although the precipitates obtained in these tests were filterable, the small scale of the experiments did not permit complete evaluation of the filtration characteristics.

Further precipitations involving 25 to 100 g of neptunium were performed to test the large-scale operability of the original precipitation procedure. In addition to pure neptunium solutions, process feed solutions containing Pu^{238}, fission products, and corrosion product contaminants were used in some of these tests. The results of the tests are summarized in Table I.

TABLE I

Scouting Tests - Neptunium Oxalate Precipitation

	Feed Composition(a)				Np Loss in Filtrate	
Run	Np, g/l	HNO_3, M	Pu^{238}, d/(min)(ml)	F.P. Activity,(b) γc/(min)(ml)	mg/l	%
1	7.3	2.12	-	-	30	0.6
2	12.2	1.21	-	-	15	0.2
3	13.0	3.09	$1.6x10^9$	$\sim10^5$	447	4.4
4	30.7	2.25	$8.6x10^8$	$\sim10^5$	140	0.8
5	30.5	2.52	$2.9x10^9$	$\sim10^5$	2000	7.7

(a) All feed solutions contained 0.05M hydrazine (partially decomposed).

(b) Fission product activity was predominately $Zr\text{-}Nb^{95}$ activity counted at 2.0% efficiency for Cs^{137} activity.

Filtrate losses of neptunium in runs 1 and 2 were relatively low. The feed solutions for these runs contained only purified neptunium, and had stood 3 and 7 days, respectively, before precipitation. Higher neptunium losses were obtained in runs 3, 4, and 5, in which process feed solutions were used. These feed solutions had stood for 7, 3, and 14 days, respectively, before precipitation; the neptunium losses increased with increasing age of the feed. Spectrophotometric examination of the high loss filtrates showed the neptunium to be present as Np(V). This finding led to the speculation that the Pu^{238} and fission product contaminants in the process solutions caused radiolytic degradation of the holding reductant, hydrazine, and led to the formation of increasing amounts of Np(V) with time. Spectrophotometric examinations of process feed solutions, however, showed that only 1 to 2% of the neptunium was present as Np(V) 3 days after preparation, and that this percentage did not increase significantly for at least 10 days. It was concluded that only small quantities of Np(V) were produced by chemical or radiolytic processes during storage, and that the larger losses were the result of degradation of hydrazine and subsequent Np(V) production during the digestion of the precipitate at 80°C. Increased loss of neptunium to the filtrates with increasing storage time was attributed to slow degradation of hydrazine during storage, with the result that less degradation during precipitation was required before Np(V) production began.

The time required for filtration of the neptunium oxalate slurries produced in these large-scale tests was longer than desired; relative filtration factors in the range of 6 to 10 were obtained. The particle size distribution of the slurries was such that small quantities of precipitate passed the 5-micron filter. Increased digestion times did not improve the filtration characteristics of the precipitate.

These tests showed that the original precipitation procedures did not meet the process requirements. Further studies were undertaken to develop suitable procedures.

REDUCTANTS FOR Np(V)

The use of a reagent for reducing Np(V) to Np(IV) in the oxalate precipitation was considered to be the most effective means of decreasing neptunium losses. A reductant was sought that would function satisfactorily under process conditions and that would not contaminate the oxide product. Ferrous ion was found to be an adequate reductant for Np(V) under process conditions, but coprecipitation of ferrous oxalate resulted in contamination of the oxide. Other metallic reductants were therefore not considered. Since the more common nonmetallic reductants were reported(5) to reduce Np(V) to Np(IV) slowly in dilute nitric acid at room temperature, a number of potential reductants were screened to determine their reducing ability under various conditions. The test conditions and results are shown in Table II. Control runs with ferrous sulfamate reductant are included for comparison.

Ascorbic acid (or isoascorbic acid) was the most effective of the reductants tested for reducing Np(V) to Np(IV). Although reduction by ascorbic acid was very slow in 1M nitric acid at room temperature, the rate of reduction increased rapidly with increasing nitric acid concentration and increasing temperature. Severe decomposition of ascorbic acid occurred in the tests with 2M nitric acid at elevated temperature, preventing complete reduction of Np(V). However, addition of a protective agent, hydrazine or sulfamic acid, stabilized the ascrobic acid and allowed complete reduction. Isoascorbic acid exhibited reducing properties similar to those of ascorbic acid.

Reduction by Ascorbic Acid

A brief study of the rate of the reduction of Np(V) by ascorbic acid was undertaken to determine conditions favoring rapid reduction and to determine the compatibility of these conditions with the oxalate precipitation. These studies were performed with purified neptunium solutions containing 1 g/l of Np(V). The test solutions were made

TABLE II

Screening Tests For Reductants

Test Solution	Reductant	Reduction Temp, °C	Reduction Time, hr	Extent of Reduction, %
1.2 g/l Np(V), 1M HNO_3	0.05M $Fe(NH_2SO_3)_2$	23	0.5	100
	0.05M $N_2H_4 \cdot HNO_3$	23	1	<1
	0.05M $N_2H_4 \cdot HNO_3$	60	0.5	<1
	0.001M $Fe(NH_2SO_3)_2$	23	1	24
	0.001M $Fe(NH_2SO_3)_2$ - 0.05M $N_2H_4 \cdot HNO_3$	23	1	24
	0.05M H_2O_2	23	3	<2
	0.05M H_2O_2	75	0.25	<2
	Saturated with SO_2	23	1	<1
	0.06M HI	23	1	2
	0.06M HI	55	0.5	6
	0.06M HI	80	0.5	13
	0.05M ascorbic acid	23	1	<5
	0.05M ascorbic acid	60	0.5	25
	0.05M ascorbic acid	80	0.5	100
	0.05M isoascorbic acid	80	0.5	100
1.2 g/l Np(V), 2M HNO_3	0.05M ascorbic acid	80	0.5	60
	0.05M isoascorbic acid	80	0.5	60
	0.05M ascorbic acid - 0.05M $N_2H_4 \cdot HNO_3$	80	0.5	100
	0.05M isoascorbic acid - 0.05M $N_2H_4 \cdot HNO_3$	80	0.5	100
	0.05M ascorbic acid - 0.05M HSO_3NH_2	80	0.5	100
	0.05M isoascorbic acid - 0.05M HSO_3NH_2	80	0.5	100
	0.05M ascorbic acid - 0.05M HSO_3NH_2	23	1	18
	0.05M ascorbic acid - 0.05M $N_2H_4 \cdot HNO_3$	23	1	18

0.05M in hydrazine immediately prior to each run to reduce any Np(VI) to Np(V) and to stabilize the reductant. Incomplete and very slow reduction of Np(V) by hydrazine was observed in these test solutions. Solutions that originally contained 100% Np(V), 0.05M hydrazine, and 0.97, 1.93, 2.89, or 3.86M nitric acid contained 1.3, 24.5, 75.7, and 96.6% Np(IV), respectively, after standing at room temperature for 10 days. The initial rate of the reduction by hydrazine in 3.86M nitric acid is shown in Table III.

TABLE III

Rate of Reduction of Np(V) at 23°C
in 3.86M Nitric Acid - 0.05M Hydrazine

Np Concentration: 1 g/l

Reaction Time, min.	Reduction, %
10	1.8
48	6.8
65	11.3
105	13.1

Rate data for the reduction of Np(V) to Np(IV) by ascorbic acid in the presence of hydrazine are shown in Figures 3 and 4. These data indicated that ascorbic acid would function satisfactorily as a reductant for Np(V) in the oxalate precipitation process and that essentially complete reduction of Np(V) could be achieved during precipitation at room temperature if the feed contained about 4M nitric acid. Alternatively, it was indicated that complete reduction could be achieved at lower acid concentrations at elevated temperatures. It was anticipated, and later observed, that the rate of reduction would be more rapid during precipitation than under the conditions of these studies, because of the additional driving force for the reduction that results from the precipitation of Np(IV).

REDUCTION PROCEDURES

Development of procedures for the reduction of Np(V) by ascorbic acid and adaptation of these procedures to the oxalate precipitation were performed in laboratory-scale and pilot-scale precipitations. In the tables of data in this section, runs with number designations refer to large-scale precipitations of about 50 g or more of neptunium. Runs designated by letter refer to laboratory-scale precipitations of about 0.5 g of neptunium. Process solutions were used in most tests; the Np(V) content of these solutions was usually 0.5 to 1.0 g/l. Precipitation procedures were developed simultaneously

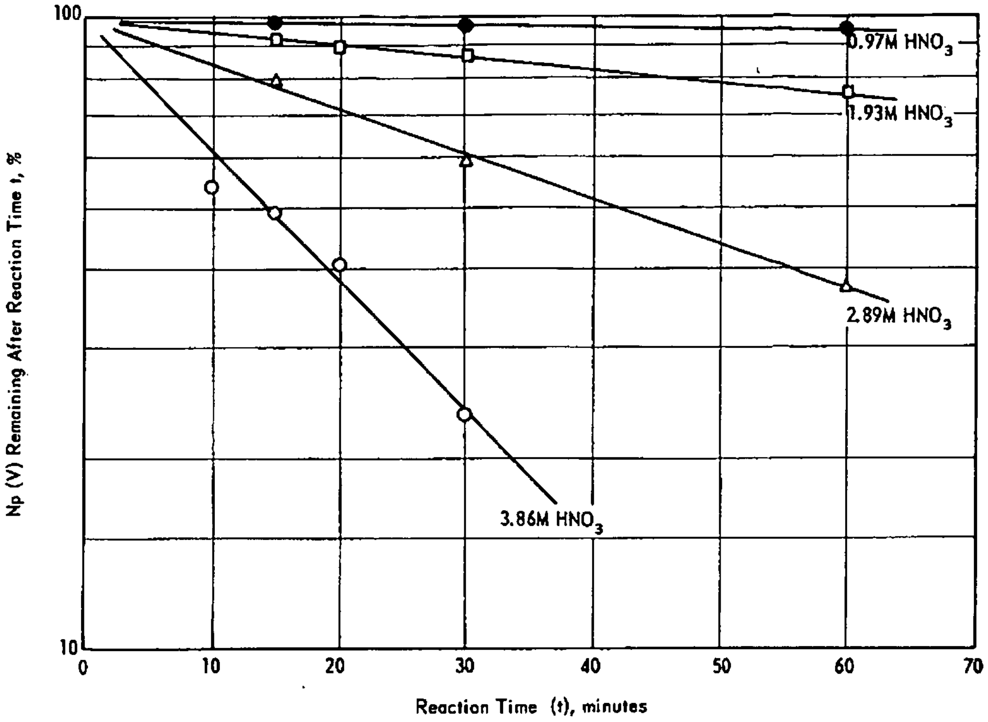

FIG. 3 THE REDUCTION OF Np(V) TO Np(IV) AT 23°C BY 0.03M ASCORBIC ACID IN NITRIC ACID-0.05M HYDRAZINE

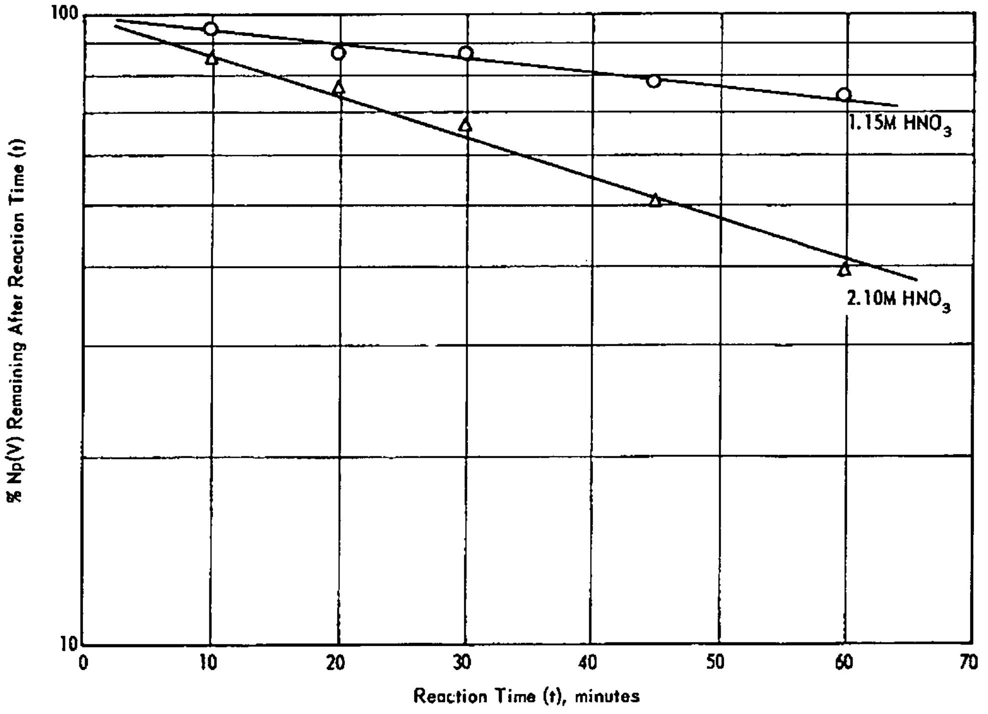

FIG. 4 THE REDUCTION OF Np(V) TO Np(IV) AT 50°C BY 0.03M ASCORBIC ACID IN NITRIC ACID-0.05M HYDRAZINE

with the reduction procedures and are reported in a subsequent section.

Effect of Hydrazine and Ascorbic Acid Concentrations

In the previous tests, low concentrations of Np(V) in 1 to 2M nitric acid were reduced rapidly at 80°C by 0.05M ascorbic acid in the presence of 0.05M hydrazine. The concentrations of reductant and stabilizer actually required for complete reduction were determined in test precipitations. In the tests, neptunium feed solutions were heated to 50°C and were adjusted to the desired concentrations of hydrazine and ascorbic acid. The solutions were then heated to 80°C and maintained at that temperature for 30 minutes to complete the reduction. After the solution was cooled to 50°C, neptunium oxalate was precipitated by adding 1M oxalic acid to the agitated solution over a period of 30 to 45 minutes until the solution contained 0.1M excess oxalic acid. The resulting slurry was digested with agitation for 30 minutes and was filtered after cooling to room temperature. The completeness of the reduction was judged from the magnitude of the filtrate losses. Control precipitations performed in the absence of reductant showed neptunium losses to the filtrates of up to 2 g/l.

The data in Table IV show that complete reduction of Np(V) in process solutions was accomplished without increasing the concentration of hydrazine. Although the 0.05M concentration of hydrazine present from the preceding anion exchange step was partially decomposed at the time of precipitation, a sufficient concentration of hydrazine still remained to protect the reductant. The data also show that a 0.03M concentration of ascorbic acid was sufficient to effect complete reduction of the Np(V) present. These tests were performed with feed solutions that were prepared by anion exchange within 2 weeks of the time of precipitation. Tests with feed solutions prepared about 4 weeks prior to precipitation showed sufficient decomposition of hydrazine and production of Np(V) to require re-establishing the hydrazine concentration and increasing the ascorbic acid concentration to 0.1M to obtain complete reduction. Solutions of 100% Np(V) required higher concentrations of hydrazine and ascorbic acid for complete reduction.

Effect of Nitric Acid Concentration and Temperature

The reduction of Np(V) by ascorbic acid was very slow at room temperature in 1 to 2M nitric acid, but was rapid at higher acid concentrations or at higher temperatures. Since it was desired to perform the oxalate precipitation at nitric acid concentrations near 1M and at moderate temperatures, tests were performed to determine the temperature and acid requirements for complete reduction of Np(V) by ascorbic acid under precipitation conditions. Test conditions and results are summarized in Table V. In all tests, a 0.03M concentration of ascorbic acid was used without additional hydrazine.

TABLE IV

Np(V) Reduction - Effect of Concentrations of Hydrazine and Ascorbic Acid

Run	Feed Composition[a] Np, g/l	Feed Composition[a] HNO_3, M	Hydrazine Added, M	Ascorbic Acid Concentration, M	Np Loss in Filtrate mg/l	Np Loss in Filtrate %
6	18.7	1.6	0.05	0.05	9.1	0.06
7	41.3	1.7	0.02	0.05	8.0	0.04
8	27.1	2.7	None	0.05	7.7	0.04
9	26.7	2.85	None	0.06	<6	0.04
10	51.4	1.6	None	0.03	<6	0.02
A	51.4	1.64	None	0.02	21.0	0.08

(a) All feed solutions were process solutions that contained $\sim 10^8$ d/(min)(ml) of Pu^{238}, 10^5-10^6 γ c/(min)(ml) of fission products, and 0.05M hydrazine (partially decomposed).

The tests demonstrated that the reduction of Np(V) by ascorbic acid was rapid and complete over a wide range of conditions that were suitable for the oxalate precipitation. The data show that the reduction was complete at either 50°C or at 80°C with feed solutions containing 1 to 3M nitric acid. The rate of the reduction was more rapid in these precipitation tests than in the rate studies; the increased rate was probably the result of the precipitation of the reduction product Np(IV). At room temperature, about 4M nitric acid was required for complete reduction. The filtration characteristics of the precipitate were poorer at the low temperature.

Degradation of Ascorbic Acid

Excessive degradation of ascorbic acid was observed in the reduction tests at 80°C. Complete reduction of Np(V) was obtained in the tests, but the degradation products of ascorbic acid caused frothing and sludge formation. The sludge could be removed from the filtered precipitate by extensive washing, but was undesirable as a potential source of contamination. The formation of sludge was reduced significantly by decreasing the ascorbic acid concentration from 0.05 to 0.03M, and was essentially eliminated by decreasing the temperature from 80 to 50°C. Further precipitations were performed to establish conditions for minimum degradation of ascorbic acid. In the tests, reductions and precipitations were performed at 50°C, and only the procedure of adding the reductant was varied. The test procedures and results are summarized in Table VI.

Degradation of the ascorbic acid reductant was very slight under all of the test conditions, but was greatest when the reductant was added 30 minutes prior to the precipitation. Reduction of Np(V) was

TABLE V

Np(V) Reduction and Oxalate Precipitation - Effect of Neptunium Concentration, Nitric Acid Concentration, and Temperature

	Feed Composition[a]		Run Conditions				Relative Filtration Factor	Np Loss in Filtrate	
Run	Np, g/l	HNO_3, M	Reduction Temp., °C	Precipitation Temp., °C	Digestion Temp., °C	Filtration Temp.		mg/l	%
10	51.4	1.64	80	50	50	Room	2.5	<6	0.02
B	26.7	2.85	80	50	50	Room	-	<6	0.02
11	25.6	1.16	50	50	50	Room	2.0	<6	0.03
12	29.3	1.30	50	50	50	Room	1.5	6.1	0.03
13	46.7	1.62	50	50	50	Room	2.3	6	0.02
14	26.7	2.52	50	50	50	Room	2.5	<6	0.01
C	26.7	2.85	50	50	50	Room	-	<6	0.02
D	25.7	5.05	Room	Room	Room	Room	-	7.9	0.04
15	21.8	4.0	Room	Room	Room	Room	4.5	<6	0.03
16	20.1	4.0	Room	Room	Room	Room	4.9	<6	0.03
E	27.2	3.1	Room	Room	Room	Room	-	38.1	0.2
F	23.3	2.1	Room	Room	Room	Room	-	>100	>0.5

(a) All feed solutions were process solutions that contained $\sim 10^8$ d/(min)(ml) of Pu^{238}, 10^5-10^6 γ c/(min)(ml) of fission products, and 0.05M hydrazine (partially decomposed).

TABLE VI

Np(V) Reduction Procedures

Run	Feed Composition[a]		Reduction Procedure	Np Loss in Filtrate	
	Np, g/l	HNO_3, M		mg/l	%
13	46.7	1.62	0.03M ascorbic acid added at 23°C, heated to 50°C (heating time: 30 min.); precipitated and digested at 50°C.	<6	0.02
11	25.6	1.16	As above.	<6	0.03
17	29.3	1.55	0.03M ascorbic acid added at 50°C after precipitation and prior to digestion.	14.0	0.08
18	28.0	1.98	As above.	9.3	0.06
12	29.3	1.30	0.03M ascorbic acid added at 50°C immediately prior to precipitation.	6.1	0.03
19	20.7	2.4	As above.	6.7	0.06

(a) All feed solutions were process solutions that contained $\sim 10^8$ d/(min)(ml) of Pu^{238}, 10^5-10^6 γ c/(min)(ml) of fission products, and 0.05M hydrazine (partially decomposed).

essentially complete with either the 30-minute reduction period or when the reductant was added immediately before precipitation at 50°C. When the reductant was added after precipitation but prior to the digestion at 50°C, reduction was slightly less complete. The procedure of adding the reductant at 50°C and performing the reduction and precipitation simultaneously was therefore considered to be optimum.

PRECIPITATION PROCEDURES

The procedure originally developed for the precipitation of neptunium oxalate did not produce the desired quality of precipitate. The combined conditions of precipitation at 23°C and digestion at 80°C did not produce a dense, granular precipitate that filtered readily. In the course of the studies of reduction procedures, the effect of process variables on the precipitation was surveyed and optimum conditions for the precipitation were determined. The quality of a precipitate formed under a given set of conditions was evaluated on the basis of filtration characteristics expressed as the relative filtration factor. Filtrations in the pilot-scale equipment were performed at a pressure of 15 inches of Hg; under these conditions water would pass through the filter at about 0.9 liters per minute. In the filtration of a slurry containing about 70 g of neptunium, a cake 1-1/2 to 2 inches thick was accumulated on the filter.

Effect of Nitric Acid Concentration and Temperature

The data in Table V are representative of nitric acid concentrations and temperatures that were examined. Precipitates formed and digested at 50°C were routinely of high quality regardless of the nitric acid concentration, as attested by relative filtration factors of 2 to 2.5. The deleterious effect of lower temperature on the quality of the precipitate is demonstrated by the relative filtration factors of 4.5 to 5 for slurries produced at room temperature. Increasing the 30-minute digestion period at room temperature from 30 to 60 minutes did not improve filtration rates. Digestion at 50°C of a slurry formed at room temperature improved filtration characteristics, but this procedure was less convenient than performing the entire operation at the elevated temperature. Waste losses of neptunium were low for all temperatures and acid concentrations that favored complete reduction of Np(V) by ascorbic acid.

Effect of Neptunium Concentration

As shown in Table V, precipitations of neptunium oxalate at 50°C from feed solutions containing 20 to 50 g/l of neptunium produced low waste losses and slurries that filtered readily. The quality of the precipitate was not affected by changes in the neptunium concentration within this range. Other tests with feed solutions containing as little as 5 g/l of neptunium also showed good results; precipitations at lower neptunium concentrations are operative but waste losses are greater. Because no undesirable trend was noted as the neptunium concentration in the feed was increased to about 50 g/l, good quality precipitates should result at even higher neptunium concentrations.

Effect of Oxalic Acid Concentration

Throughout these studies 1M oxalic acid was used as the precipitant and was found to be satisfactory. This concentration of precipitant was sufficiently high to minimize waste volumes and, at the same time, was not so high as to require precise control of the addition rate. In most precipitations, sufficient oxalic acid was added to precipitate the neptunium and to establish a 0.1M excess of oxalic acid in the final slurry. The 0.1M excess was adopted on the basis of the solubility data, which indicated that this concentration produced a minimum solubility of neptunium under the process conditions. In the course of the tests, however, the oxalic acid excess was varied from 0.05 to 0.15M without significant loss of neptunium; this demonstrated that the solubility of neptunium oxalate is not highly sensitive to the oxalic acid concentration under the process conditions.

Effect of Rate of Agitation

Tests of the effect of the rate of agitation on the quality of the precipitate were performed in the pilot-scale precipitator, which had a 3-inch-diameter agitator. Varying the operating speed of the agitator between 200 and 450 rpm produced no observable change in the precipitate. The precipitation was therefore shown to be generally insensitive to the rate of agitation within a practical range of speeds that assured good mixing.

WASHING AND DRYING OF PRECIPITATE

The filter cakes of neptunium oxalate were usually washed with about 3 cake volumes of 1 to 2M nitric acid - 0.1M oxalic acid. The wash solution was divided and used in 3 portions to increase the efficiency of the washing. The composition of wash solution was selected to minimize solubility losses of the product. In practice, the neptunium loss in the washing step was significantly less than the equilibrium solubility of neptunium oxalate because of the short contact time of the solution with the precipitate. The washed cakes were dried by drawing ambient air through the cake. After about 30 minutes, the surface water content of good quality cakes was reduced to 3 to 30 wt %, with an average of about 12 wt %. The water content of poor quality cakes ranged up to 50 wt %. Essentially complete removal of surface water could be accomplished by extended air drying, but this was not required prior to calcination of the cake to the oxide. The bulk density of completely air-dried precipitate was about 1 g/cc.

DISPOSAL OF FILTRATE AND WASH WASTES

The filtrate and wash wastes from the precipitation of neptunium oxalate normally contained less than 10 mg/l of neptunium. Recovery of neptunium from these wastes, when required, was readily accomplished by anion exchange after simple acid and valence adjustments. The oxalic acid present in the waste did not interfere with the recovery procedure, and decomposition of the oxalate was unnecessary. The waste was adjusted to 8M nitric acid and made 0.05M in ferrous sulfamate to reduce Np(V) to Np(IV). After a 30-minute reduction period, the excess reductant was oxidized by heating the solution at 55°C for 30 minutes. Neptunium was recovered from this solution by absorption of the anionic nitrate complex on a bed of "Dowex" 1-X4, 50-100 mesh resin. After the loaded resin bed was washed with 8M nitric acid, the neptunium was eluted from the resin with 0.35M nitric acid.

RECOMMENDED PROCESSES

From the results of the development studies, two general procedures for the preparation of neptunium oxalate were formulated. The preferred procedure requires operation at an elevated temperature; the alternative procedure is operative at room temperature. Both procedures are designed for feed compositions that result from anion exchange preparation of the feed, i.e., solutions containing more than 5 g/l of Np(IV) in about 1M nitric acid and stabilized with 0.05M hydrazine to suppress the formation of Np(V). The procedures are summarized below.

Precipitation at Elevated Temperature

1. The feed solution (1-4M in nitric acid) is heated to 50 ±5°C and is agitated at a rate sufficient to ensure good mixing.

2. The feed solution is adjusted to 0.05M ascorbic acid (or isoascorbic acid). Immediately afterwards, a sufficient volume of 1M oxalic acid is added at a controlled rate over a 30- to 45-minute period to precipitate the neptunium and establish a 0.1M excess of oxalic acid in the slurry.

3. The slurry is digested at 50 ±5°C, with agitation, for 30 minutes.

4. The slurry is cooled to room temperature and filtered.

5. The precipitate is washed on the filter frit with approximately three cake volumes of 2M nitric acid - 0.1M oxalic acid. The wash solution is divided and used in three portions.

6. The washed cake is dried by drawing ambient air through the cake for 30 minutes.

7. The filtrate and wash solutions are sent to waste or are recovered by anion exchange after acid and valence adjustments.

Precipitation at Room Temperature

1. The feed solution is made at least 4M in nitric acid.

2. The adjusted feed is made 0.05M in ascorbic acid (or isoascorbic acid) and is allowed to stand for 30 minutes.

3. The solution is agitated and a sufficient volume of 1M oxalic acid is added at a controlled rate over a 30- to 45-minute period to precipitate the neptunium and establish a 0.1M excess of oxalic acid in the slurry.

4. The slurry is digested, with agitation, for 30 minutes and is then filtered.

5. The precipitate is washed and air dried, and the waste solutions are handled as in the elevated temperature procedure.

Precipitation at the elevated temperature is preferred because of its superior performance and insensitivity to process variables. This procedure normally requires no adjustment of acid in the feed, while the procedure at room temperature requires adjustment to assure complete reduction of the Np(V) present. The increased feed volume resulting from this acid adjustment leads to a greater total loss of product to the filtrate, and an increased volume of waste is generated. Also, precipitates formed at the elevated temperature can be filtered in about one-half the time required for precipitates formed at room temperature, and can be washed and air dried more easily.

DECONTAMINATION PERFORMANCE

The effectiveness of the oxalate precipitation in decontaminating neptunium from the major radioactive impurities present in process solutions is shown in Table VII. No significant separation from plutonium or from the Pa^{233} daughter of Np^{237} was achieved. Significant decontamination from zirconium-niobium was obtained with decontamination factors averaging about 40 when the neptunium feed contained zirconium-niobium activity at a level of 10^5-10^6 γ c/(min)(ml). The levels of other fission products in the feed solutions were usually too low for accurate measurement, but the decontamination factors for cerium and ruthenium were estimated to be less than 10 and greater than 100, respectively.

TABLE VII

Decontamination of Neptunium in Process Feed Solutions by Oxalate Precipitation

	Feed Composition[a][b]					Decontamination Factor		
Run	g/l	HNO_3, M	Pu^{238}, d/(min)(ml)	Pa^{233}, γ c/(min)(ml)	Zr-Nb^{95}, γ c/(min)(ml)	Pu	Pa	Zr-Nb
11	25.6	1.16	3.94×10^8	9.0×10^4	3.1×10^4	~1	~1	3
20	28.0	2.45	1.78×10^9	1.5×10^5	1.4×10^6	~1	~1	23
12	29.3	1.30	2.26×10^8	1.5×10^5	3.2×10^6	~1	~1	12
19	20.7	2.40	5.05×10^8	1.7×10^5	5.2×10^6	~1	~1	42
21	24.0	2.39	5.74×10^8	8.4×10^4	6.2×10^6	~1	~1	56
14	26.7	2.52	1.10×10^9	8.3×10^4	7.7×10^6	~1	~1	33

(a) All feed solutions contained 0.05M hydrazine (partially decomposed).
(b) Gamma activities determined at 2.0% counting efficiency for Cs^{137} activity.

Laboratory tests with individual radioactive contaminants in pure neptunium feed solutions were performed to measure the extent of decontamination attainable when neptunium oxalate was precipitated under various conditions. Individual contaminants were added to 30 g/l neptunium solutions after acid adjustment and allowed to stand for at least 24 hours before precipitation. This period permitted equilibration of the contaminant element among its various species, but exact duplication of the species present in process solutions could not be assured. The precipitations were performed with 0.5g of neptunium under four conditions - in 1M and 2M nitric acid at 50°C, and in 3M and 4M nitric acid at 23°C by the procedures already described. Filtrate losses of neptunium were low in all tests except those at 23°C in 3M nitric acid, where reduction of Np(V) by ascorbic acid was only about 90% complete. The test results shown in Table VIII are in agreement with process experience. Essentially no decontamination of neptunium from plutonium, rare earths, or protactinium was achieved by oxalate precipitation. The tests showed good decontamination from ruthenium; the decontamination factor decreased with decreasing acidity and with increasing temperature. The decontamination factors for niobium and zirconium were 40 and 3, respectively; both were insensitive to the precipitation conditions.

CONVERSION OF NEPTUNIUM OXALATE TO NEPTUNIUM OXIDE

CALCINATION PROCEDURE

Material balance calculations for the oxalate precipitation, and thermogravimetric analyses of air-dried neptunium oxalate showed its composition to be $Np(C_2O_4)_2 \cdot 6H_2O$. When this compound was heated in

TABLE VIII

Decontamination of Neptunium in Simulated Process Feed Solutions by Oxalate Precipitation

Precipitation Conditions		Decontamination Factors[(a)]						
HNO_3 Conc., M	Temp., °C	Pu^{238}	Pa^{233}	$Ce\text{-}Pr^{144}$	Ru^{103}	Nb^{95}	Zr^{95}	$Zr\text{-}Nb^{95}$
4.0 - 4.3	23	~ 1	~ 1	~ 1	1000	40	3	5
3.0 - 3.3	23	~ 1	~ 1	~ 1	450	40	3	5
1.7 - 2.0	50	~ 1	~ 1	~ 1	450	40	3	5
1.0 - 1.3	50	~ 1	~ 1	~ 1	200	40	3	5

(a) Activity of contaminants in test solutions:

Pu^{238} - 2×10^6 α d/(min)(ml)
Pa^{233} - 4×10^5 β c/(min)(ml)
$Ce\text{-}Pr^{144}$ - 5×10^5 β c/(min)(ml)
Ru^{103} - 5×10^5 γ c/(min)(ml)
Nb^{95} - 2×10^5 γ c/(min)(ml)
Zr^{95} - 6×10^4 γ c/(min)(ml)
$Zr\text{-}Nb^{95}$ - 5×10^5 γ c/(min)(ml)

Gamma activities determined at 2.0% counting efficiency for Cs^{137}

Beta activities determined at 5.7% counting efficiency for Ra D and E

air at a rate of 5 to 6°C per minute, a weight loss corresponding to 6 moles of water per mole of neptunium occurred between 90 and 285°C, indicating the formation of anhydrous $Np(C_2O_4)_2$. Further heating led to the rapid conversion of $Np(C_2O_4)_2$ to NpO_2 at 330 ±5°C. Heating the oxide to 800°C resulted in no further weight change, demonstrating completeness of the conversion and the stability of the product. Chemical and X-ray diffraction analyses of the product showed the composition to be NpO_2.

Neptunium oxide was prepared in the pilot tests by the following procedure. Partially air-dried neptunium oxalate was heated under a stream of air or nitrogen from room temperature to 150°C over a 1-hour period. The temperature was maintained at 150°C for 1 hour, after which it was increased to 500 to 550°C over a 1-hour period and was maintained for 2 hours. The product was cooled to room temperature under the gas stream.

PRODUCT QUALITY

The neptunium oxide prepared in the pilot tests was dark olive in color, was free flowing, and had an average bulk density of 2.5 g/cc. Oxide produced from process feed solutions contained low levels of fission products and up to several tenths of one per cent of plutonium and of other metallic contaminants. The purity of the oxide was quite variable because it was dependent upon the purity of the feed. Product quality was not affected by the method of oxalate precipitation. Oxide produced by calcination in a nitrogen atmosphere was darker in color than that produced in an air atmosphere, but there was no detectable difference in quality.

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DP-591, PRECIPITATION OF NEPTUNIUM OXALATE AND CALCINATION TO NEPTUNIUM OXIDE

by J. A. Porter

The process for precipitating neptunium oxalate and calcining the oxalate to neptunium oxide was developed at SRL to meet the requirements for the interim production of Pu^{238} and to serve later as the finishing process for Np^{237} in plant facilities. About 5 kg of NpO_2 was produced successfully by the oxalate process in the Laboratory's facilities. Experience with the process in the Plant has been excellent since startup and NpO_2 has been produced without difficulty.

[redacted]

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