



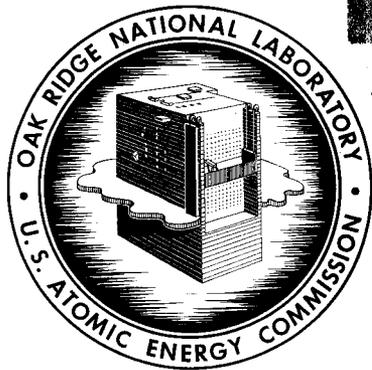
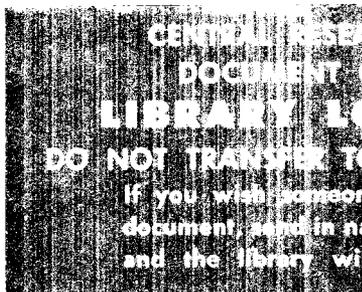
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ORNL-3055  
UC-4 - Chemistry

RECOVERY OF Np-237 BY AN  
OXIDATION-REDUCTION FLUORIDE  
PRECIPITATION METHOD

R. D. Baybarz



**OAK RIDGE NATIONAL LABORATORY**

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FLUORIDE PRECIPITATION METHOD

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### ABSTRACT

Several hundred grams of Np-237 in nitric acid solution was ~95% recovered as  $\text{NpO}_2$  of >99.5% purity. The remaining 5% was recovered as a nitric acid solution of 99.95% purity. The neptunium was oxidized to the soluble +6 state with sodium bromate, and Pu(IV), thorium, and other impurities in the solution were precipitated as fluorides. The neptunium was then reduced to Np(IV) with sulfur dioxide and precipitated as  $\text{KNpF}_5$ , dissolved in nitric acid, precipitated as neptunium oxalate, and calcined to the oxide. The recovered material balance was 99.91% with a process loss of 0.09%.

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## 1.0 INTRODUCTION

A method is described by which neptunium-237 was recovered from a nitric acid solution and converted to the oxide. The neptunium solution was the raffinate from a tributyl phosphate extraction process, in which uranium had been recovered (1). It contained small amounts of uranium, thorium, plutonium, fission and corrosion products, and process chemicals. A neptunium oxide product of >99% purity was desired.

## 2.0 FLOWSHEET

Since the chief contaminants in the neptunium feed solution were thorium, uranium, and corrosion products, the fluorides of all of which are relatively insoluble, a fluoride precipitation method for removing them was adopted. Neptunyl fluoride remains in solution under the precipitation conditions used. Neptunium is quickly oxidized to the +6 state with bromate at room temperature; plutonium oxidation is slow, and plutonium tetrafluoride and thorium tetrafluoride are immediately precipitated with hydrofluoric acid. Neptunium in the filtrate is reduced to Np(IV) with gaseous sulfur dioxide, and potassium neptunium fluoride is precipitated. The  $\text{KNpF}_5$  double salt is used because of its lower solubility than neptunium tetrafluoride, ~10 vs 50-100 mg/liter.

The neptunium precipitate is dissolved in 8 M nitric acid saturated with boric acid, and reprecipitated as the oxalate which is calcined to  $\text{NpO}_2$ .

## 3.0 EXPERIMENTAL WORK

Solution containing several hundred grams of neptunium, which had been extracted with tributyl phosphate for recovery of uranium and removal of thorium, was processed to produce a high purity oxide. A typical run (Fig. 1) consisted of concentration of the neptunium solution and acid removal by evaporation; oxidation and fluoride precipitation of thorium; reduction and precipitation of neptunium as  $\text{KNpF}_5$ ; dissolution of  $\text{KNpF}_5$ ; precipitation of neptunium oxalate; and calcination of the oxide. The original feed (Table 1) had a nitric acid concentration of 11 M and the average neptunium concentration was 3 g/liter. Evaporation to a neptunium concentration of 28 g/liter and acid concentration of ~6 M permitted handling the neptunium in a 2- by 3-ft glove box.

The concentrated neptunium solution was diluted with water to 3 M nitric acid, and to the cold (23°C) solution, solid sodium bromate was added to 150% of the stoichiometric amount to oxidize the neptunium (2).

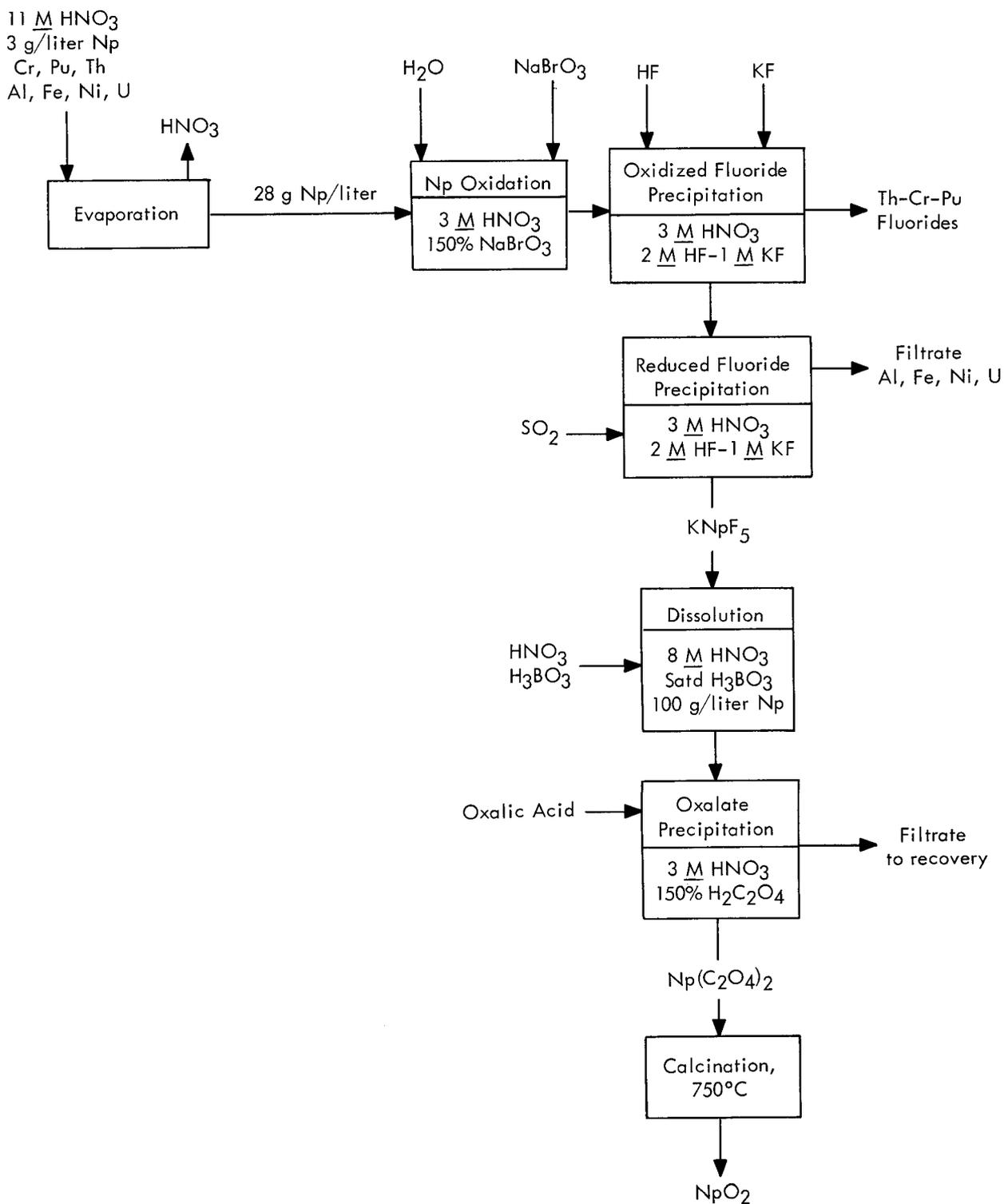


Fig. 1. Laboratory purification of Np-237.

Table 1. Neptunium Feed Solution

Element	Amount, g/liter	Element	Amount, g/liter
Np	3.06	Fe	0.54
Th	0.89	Mg	0.002
U	3.20	Mn	0.007
Al	0.38	Ni	0.05
Cr	0.11	Pu	0.005
Cu	0.003	HNO <sub>3</sub>	11 <u>M</u>

The solution was stirred 5 min and 48% hydrofluoric acid (analytical grade) was added to 2 M plus solid potassium fluoride to 1 M. The resulting thorium chromium plutonium fluoride precipitate was allowed to settle 6 hr and then was filtered on a polyethylene Buechner funnel with Whatman No. 2 filter paper and washed with 4 volumes of 0.1 M hydrofluoric acid. Through the combined filtrate and washings gaseous sulfur dioxide was bubbled to reduce the neptunium to the +4 state and precipitate K<sub>2</sub>NpF<sub>6</sub>, the sulfur dioxide flow being continued until the neptunium had completely precipitated. The potassium neptunium fluoride precipitate was allowed to settle 6 hr and was then filtered on filter paper in a polyethylene Buechner funnel. The filtrate (containing aluminum, uranium, copper, iron, nickel, and manganese) was in most cases low enough in neptunium content to be discarded (<10 mg/liter).

The potassium neptunium fluoride was dissolved with 8 M nitric acid saturated with boric acid. The K<sub>2</sub>NpF<sub>6</sub> salt is more difficult to dissolve than NpF<sub>4</sub>, but it does dissolve in 6 hr in 8 M nitric acid-saturated boric acid at 23°C to a neptunium concentration of approximately 100 g/liter.

Neptunium oxide was prepared by precipitating neptunium oxalate and calcining. The 8 M nitric acid-saturated boric acid solution containing the purified neptunium was diluted with water to 3.0 M nitric acid. A saturated solution of oxalic acid (23°C) was added drop by drop to the neptunium nitrate solution with rapid stirring until seeds of neptunium oxalate had formed. The remainder of the oxalic acid was then added in a

slow stream with rapid stirring until 150% oxalic acid was added. A fine, granular, light-green precipitate formed; 8 hr digestion was necessary to complete the precipitation. In 3.0 M nitric acid the neptunium oxalate solubility was approximately 400 mg/liter. The neptunium oxalate was filtered through a fine glass frit, washed with 0.25 M oxalic acid, and dried with absolute alcohol and acetone.

After being air-dried, it was packed into a porcelain crucible and inserted in an electric furnace. The temperature was raised to 300°C and held there 1 hr to decompose the oxalate. The temperature was then raised to 750°C and held for 4 hr to ensure conversion of the oxalate to the oxide. The resultant oxide was a light-brown, dense material (Table 2).

Table 2. Neptunium Oxide Purity Analysis

Density: 10.3 g/cc

Impurity	Amount, ppm	Impurity	Amount, ppm
Th	950	Mn	<100 <sup>a</sup>
U	600	Mo	<200 <sup>a</sup>
Pu	1020	Ni	<500 <sup>a</sup>
Al	<200 <sup>a</sup>	Si	nil
Cr	<100 <sup>a</sup>	Sn	nil
Cu	<100 <sup>a</sup>	Zn	nil
Fe	<700 <sup>a</sup>	Zr	nil
Mg	<600 <sup>a</sup>		

<sup>a</sup>Maximum values from spectroscopic analysis. The values may be a factor of 5-10 high due to the large dilution necessary to prevent interference from neptunium.

Material Balance

The material balance through the process was 99.91%, with an irrecoverable loss of 0.09%.

### Recycle Runs

Of the neptunium that was processed, 7.86% of the material had to be recycled. The highest process loss, 5.3%, was during one fluoride precipitation of impurities. This material, of which the constituents were 89% thorium and 10% chromium, was easily recovered by leaching with 4 M nitric acid—saturated boric acid at 23°C for 1-2 hr. The chromium, neptunium, and plutonium fluorides quickly dissolved, leaving the solid thorium tetrafluoride. The neptunium was recovered from the solution by an oxidation-reduction fluoride-precipitation method similar to the original flowsheet.

In one of the runs the solubility of the neptunium fluoride was exceptionally high (~400 mg/liter). The solution was recovered by carrying the neptunium on a calcium fluoride precipitate. The neptunium remaining in solution was less than 0.2 mg/liter and the filtrate was discarded. The calcium-neptunium fluoride precipitate was dissolved in 4 M nitric acid—saturated boric acid, and the neptunium was recovered by oxidation reduction—fluoride precipitation, similar to the original flowsheet.

The oxalate filtrate on hand after the oxalate precipitation contained several g of neptunium in 2.7 M nitric acid. The solution was evaporated and the acidity was decreased to 0.5 M with sodium hydroxide. The neptunium was precipitated from this solution as the oxalate, and the filtrate, containing <5 mg of neptunium per liter, was discarded.

The neptunium oxalate and the neptunium fluorides recovered from the thorium fluoride and potassium neptunium fluoride filtrates in the recycle run were combined, and the neptunium oxalate and fluorides were metathesized with 1.0 M sodium hydroxide at 90°C for 10 hr. The converted hydroxides were washed with water, and the resulting precipitate was dissolved in dilute nitric acid. The nitric acid solution of neptunium was stored as a neptunium product. The purity of the solution was 99.95%.

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