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PRODUCTION OF NEPTUNIUM METAL
ON A 100-400 GRAM SCALE

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PRODUCTION OF NEPTUNIUM METAL ON A 100-400 GRAM SCALE

D. L. Baaso, W. V. Conner, and D. A. Burton

Abstract. Procedures are described for the production of neptunium metal from neptunium oxide, and for the recovery of neptunium from reduction residues. Reduction yields ranged from 85.3% to 99.1%. High yields were obtained when 30% excess of calcium and 0.25-0.35 mole I_2 per mole of Np were used. Neptunium recovery was performed by nitric acid dissolution, anion exchange, and oxalate precipitation.

INTRODUCTION

Studies were initiated to develop a capability for producing neptunium metal. Although neptunium metal has been produced elsewhere and has been reported in the literature, procedures had to be adapted to the equipment in use at Rocky Flats.

The method chosen for metal production is similar to that reported by LASL.¹ This method consists of hydrofluorinating neptunium dioxide, and reducing the resulting neptunium tetrafluoride to the metal using calcium metal and iodine. The LASL report described 20-gram reductions, whereas the quantities desired at Rocky Flats were 100-400 grams.

This report describes the development work and production of neptunium metal in 100-400 gram batches. Reduction yields and impurity analyses of each metal button are reported.

SUMMARY

Neptunium metal was prepared successfully on a 100-400 gram scale. The neptunium was received as oxide and converted to neptunium tetrafluoride with hydrogen fluoride. Conversions as high as 100% were obtained at 650°C with an HF flow rate of 3-4 l/min. The length of hydrofluorination was varied from 4.5 to 8 hours.

The NpF_4 was reduced to metal using calcium metal as the reductant. Iodine was added to the reduction charge to increase the heat available during the reduction and yield a more fluid slag. Reduction yields of 99% were obtained using a 30% excess

of Ca and 0.25-0.35 mole I_2 /mole Np. The average yield for 10 reductions was 94.0%. This included one reduction made with a 16% excess of Ca and 0.07 mole I_2 /mole Np which resulted in a 85.3% yield, and a second reduction which resulted in a 76.5% yield for no apparent reason. Excluding these two low yields, the average yield for the remaining 8 reductions was 97.3%. The purity of the metal from all 10 reductions was high. One button contained 1000 ppm Ca, but this could have resulted from residual calcium on the surface of the button. The total impurities in the other 9 buttons ranged from 179 to 645 ppm.

The reduction residues were processed and the neptunium recovered and purified. The residues were dissolved in HNO_3 with $Al(NO_3)_3$ added to complex fluoride. The solutions were adjusted to 8N nitric acid. A valence adjustment was made to convert all neptunium to Np^{+4} , and the neptunium loaded on anion resin. After washing, the neptunium was stripped with dilute nitric acid, precipitated as oxalate, and calcined to the oxide. Overall neptunium recovery was 98.7%.

EXPERIMENTAL

The work described in this report was performed in hoods and a glovebox designed for ^{235}U processing (see Figure 1). The loading of the hydrofluorination boats, preparation of the reduction charges, and separation of the reduction products were performed in the glovebox. The hydrofluorination, reduction, and button cleaning operations were performed in hoods.

With the exception of the first run, the neptunium oxide was used as received. In the first run, neptunium oxide was purified for removal of gamma emitters by dissolution and solvent extraction techniques. The purified neptunium was then precipitated as the oxalate and calcined to oxide at approximately 650°C.

The hydrofluorination was performed in a horizontal tube furnace (see Figure 2). The furnace is equipped with HF, air, and N_2 supply lines and an HF offgas

FIGURE 1. Glovebox and Hoods Used for Np Processing.

FIGURE 2. Hydrofluorination Boat and Furnace.

FIGURE 3. Hydrofluorination Furnace and Offgas Piping.

and disposal system (see Figure 3). The heated section of the furnace is approximately 24 inches long and will accommodate two 4 inch by 8 inch by 2 inch Inconel boats. Each boat will hold up to 600 grams of oxide.

A layer of neptunium oxide, approximately $\frac{1}{8}$ inch to $\frac{1}{4}$ inch thick, was placed in the bottom of an Inconel boat. The boat was placed in the furnace and the furnace was sealed. The furnace was then heated to 650°C and a mixture of anhydrous HF and air passed over the oxide. The mixture used was 3-4 l/min. HF and 1 l/min. air. The length of the hydrofluorination cycle was varied depending on the size of the batch and visual observations of the completeness of conversion. The furnace was opened once during the hydrofluorination cycle and the material was raked to expose the bottom layer of oxide.

The NpF_4 was reduced to metal using calcium as the reductant. Iodine was added to the charge to increase the heat available during the reduction and yield a more fluid slag. The reduction vessel consisted of a MgO crucible which was placed in a stainless steel pressure vessel (see Figure 4). The annulus between

the crucible and pressure vessel was filled with MgO sand. Sand which fell inside the crucible was removed by vacuuming. A copper gasket was used to obtain a seal between the pressure vessel and pressure vessel lid.

The NpF_4 was mixed with Ca and I_2 and the mixture placed in the crucible. A top dressing of Ca and I_2 was placed on the main charge, and a MgO lid was placed on the crucible. The pressure vessel was sealed and leak-checked alternately under 15 inches Hg vacuum and 15 psig argon. It was then evacuated to 15 inches Hg and backfilled to 15 psig argon three times to purge all air from the vessel. After the last backfill, the pressure was reduced to 3 psig. The pressure vessel was placed in the induction furnace and heated until the charge reacted. The reaction usually initiated after 5 minutes of heating. The occurrence of the reaction was determined by a heat spike on the temperature recorder. The thermocouple was located in a well along the outside wall of the pressure vessel, and the charges reacted when the temperature recorder reached 550 - 650°C . After the reaction occurred, heat was maintained for an additional 10 minutes to ensure maximum separation of neptunium metal from the slag.

FIGURE 4. MgO Crucible and Lid, Stainless Steel Pressure Vessel and Lid.

After the pressure vessel had cooled, it was opened and the neptunium button was separated from the slag and crucible. The button was pickled in 2N HNO₃ for 5 minutes, water washed and then dried.

RESULTS AND DISCUSSION

HYDROFLUORINATION

The NpO₂ was converted to NpF₄ according to the following equation.

Neptunium oxide is dark brown and the tetrafluoride is light green. Any appreciable quantities of unconverted oxide are easily detectable in the light green

tetrafluoride. Therefore, visual observations are quite useful during the course of the hydrofluorination step in determining if the oxide is fully converted. The weight gained during the hydrofluorination step is a more accurate method for determining the completeness of conversion. The values for percent conversion given in this report are based on weight changes.

The length of hydrofluorination was varied from 4 hours to 8 hours. The time required for good (>90%) conversion varies depending on the amount and the reactivity of the oxide being processed. Most batches were converted after 4-5 hours of hydrofluorination. However, one batch containing 168 grams of NpO₂ required 8 hours of hydrofluorination to achieve a 90% conversion. A summary of the hydrofluorination results and conditions is given in Table I.

TABLE I. Hydrofluorination Results and Conditions.

Batch No.	NpO ₂ Weight (g)	NpF ₄ Weight (g)	% ¹ Conversion to NpF ₄	Hydrofluorination Time (hours)
1	*	*	*	*
2	105.6	*	*	6
3	379	437	93	7
4	124.8	145.2	100	4
5	129	149	98	4
6	168	184.5	90	8
7	458.5	513.5	76	4.5
8	113	130	100	4.5
9	299.5	342.5	97.5	5
10	239.5	279.5	100	5

* Data not accurately recorded.

$$^1\% \text{ Conversion} = \frac{\text{Actual Weight Change}}{\text{Theoretical Weight Change}} \times 100$$

REDUCTION TO METAL

The NpF₄ was reduced to metal according to Equation 2.

The first reduction charge was prepared with a 16% excess of calcium and 0.07 mole I₂/mole Np. This charge produced an 85.3% yield. The low yield is attributed to a miscalculation which resulted in the quantities of Ca and I₂ being too low. This condition was corrected in subsequent reductions. Reductions 2 through 4 were made using a 30-50% excess of Ca and 0.25 mole I₂/mole Np. Reductions 2 and 3 produced good (>98%) yields, but reduction 4 produced a 76.5% yield, for no apparent reason. Subsequent reductions were made using 0.35 mole I₂/mole Np for charges containing less than 200 grams of Np, and 0.25 mole I₂/mole Np for charges containing more than 200 grams of Np.

The conversion of the oxide used for reduction 7 was only 76% complete. The reduction charge contained 400 grams of Np and produced a 97% yield in spite of the poor conversion. A summary of the data from 10 neptunium reductions is given in Table II. The reduction numbers in Table II can be directly related to the batch numbers in Table I. Single button yields of 99% Np were obtained using the procedure described. The average yield for all 10 reductions was 94.0%. Excluding the two low-yield reductions (1 and 4), the average yield for the 8 remaining reductions was 97.3%. The photograph of a typical 300-gram Np button (No. 3) is shown in Figure 5.

TABLE II. Reduction Data.

Reduction No.	Np Weight In Charge (g)	Button Weight (g)	Metal Yield (%)	% Excess of Ca	Moles I ₂ / Mole Np
1	102	87	85.3	16	0.07
2	90.9	90	99.0	56	0.26
3	334	328	98.2	29	0.28
4	110	84.1	76.5	30	0.25
5	119	107.8	98	30	0.35
6	138.7	133.4	96.2	30	0.35
7	401.9	389.5	96.9	30	0.25
8	98.4	92.2	93.6	30	0.35
9	125.6	121.5	96.7	30	0.35
10	344.4	343.3	99.7	30	0.25

The purity of the buttons was greater than 99.9% Np in all cases but one. Button No. 3 contained 1000 ppm Ca, but the high value could have resulted from residual calcium on the surface of the button. Impurity data for the buttons are summarized in Table III. Only major impurities are reported, but the total includes all detectable impurities.

TABLE III. Major Button Impurities (ppm).

Button No.	Ag	Al	Ca	Cr	Fe	Mg	Mn	Ni	Si	Total
1	15	13	75	62	84	25	15	214	84	587
2	3	11	50	36	89	50	15	97	63	414
3	1.5	14	1000 ¹	40	53	10	6	27	101	1252
4	<2.5	26	30	19	94	60	3	29	178	490
5	<2.5	16	30	12	268	30	3	28	219	645
6	<2.5	171	20	27	187	3	2	46	50	521
7	<2.5	13	<10	15	43	25	<2	21	62	179
8	*	*	*	*	*	*	*	*	*	*
9	*	*	*	*	*	*	*	*	*	*
10	<2.5	30	<10	14	64	15	<2	30	190	352

* Button not sampled.

¹The Ca impurity may have resulted from residual calcium on the surface of the Np button. It should distill off in casting.

REDUCTION RESIDUES RECOVERY

The reduction residues were slowly fed into 16N HNO₃ at 100°C. Feeding MgO sand, crucible, and CaF₂ slag to HNO₃ must be done at temperatures in excess of 90°C and with freeboard space equal to 3 volumes of the HNO₃ because of the violent reaction between MgO and HNO₃. After the addition of the solids was complete, more HNO₃ was added, and the solution was mixed for one hour at 100°C. Sixty percent aluminum nitrate solution was then added to complex the fluoride, and mixing continued another 15 minutes. Water was added to keep the solution from salting out. The liquid-to-solids ratio used was 1.5 liters 16N HNO₃ + 1.8 liters H₂O per 400 grams

FIGURE 5. 328-Gram Neptunium Button.

MgO, 1 liter 16N HNO_3 per 600 grams of slag, and 1 liter of 60% $\text{Al}(\text{NO}_3)_3$ solution per 200 grams of slag. The addition of H_2O and $\text{Al}(\text{NO}_3)_3$ was delayed for the purpose of keeping the H^+ high and the F^- uncomplexed during the first hour of dissolution. $\text{Al}(\text{NO}_3)_3$ should be added with the solution at reflux temperature and refluxed for ~15 minutes. The solution was filtered through a medium glass frit.

The leach solutions were adjusted to 8N H^+ . The feed solutions were made 0.1M in ferrous sulfamate to reduce the Np^{+5} to Np^{+4} and allowed to stand for approximately one hour. Upon adding ferrous sulfamate, considerable offgassing was observed. This was probably due to the reaction of nitrite ion with sulfamate. The feed solution was ion exchanged at 25°C on Dowex 1-x4 anion resin.

One liter of Dowex 1- $\times$ 4 anion resin was used per 25 grams of Np. During the ion exchange step, gassing of the column presented some problems. The ion column was being fed from top to bottom. The offgassing was disturbing the resin bed and forcing it upward. There were large gas pockets in the column. A glass-wool plug on top of the resin had to be held down mechanically. Because of the offgas problem, a desired mass loading rate of 10 mg Np/minute/cm² could not be obtained. It is recommended that future ion exchange of Np using ferrous sulfamate be done using a flow from bottom to top. Another possible alternative is to try outgassing the solution by boiling and cooling it just prior to valence adjustment and loading.

The column was washed with 8 column-volumes of 8N HNO₃ + 0.05N ferrous sulfamate followed with 2 column-volumes of 8N HNO₃. A line sample was taken after each column-volume and the results are found in Table IV.

TABLE IV. Ion Column Wash Data (mg/l)

Column- Volume No.	Ca	Fe	Mg	Mn	Si
1	40	400	200	4	10
2	20	400	100	4	6
3	10	400	20	4	6
4	<2	200	10	2	8
5	<2	400	6	4	2
6	<2	200	6	2	6
7	<2	400	4	2	6
8	<2	600	8	4	6
9	<2	<2	6	<2	2
10	<2	<2	4	<2	4

The Fe and Mn impurities in washes 1 through 8 are attributed to the ferrous sulfamate in the wash. It

is seen from this data that 4 column-volumes of wash are sufficient to remove impurities.

The ion column was eluted with 0.35N HNO₃ at a flow rate of 0.5 ml/min./cm² of column area. The eluate was concentrated by evaporation. The acidity was then adjusted to 3-4N H⁺ and a 10% excess of ascorbic acid added to reduce Np⁺⁵ to Np⁺⁴. The neptunium was then precipitated with 1M oxalic acid at 50°C.² Precipitation was not complete after 30 minutes digestion (post precipitation was noted after 16 hours digestion at room temperature), and additional ascorbic acid was required. After final precipitation, neptunium losses in the filtrate were 5.2 mg per liter. These losses compare favorably with those reported by Porter.³

Neptunium recovery was 98.7%, and the calcined neptunium oxide was determined to be 87.7% Np by emission spectroscopy. Spectrographic analyses indicated that principal impurities were Al - 21 ppm, Ca - 2500 ppm, Cr - 17 ppm, Fe - 45 ppm, K - 25 ppm, Mg - 20 ppm, Mn - 11 ppm, Ni - 30 ppm, Si - 97 ppm. The impurities totaled 2780 ppm.

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