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# Lab Scale Production of $\text{NpO}_2$

by

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## **Lab Scale Production of NpO<sub>2</sub>**

Authors: M.G. Bronikowski, J.M. Duffey, and R.R. Livingston

**August 2003**

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**Westinghouse Savannah River Company  
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## Lab Scale Production of $\text{NpO}_2$

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### ABSTRACT

The Savannah River Site (SRS) plans to disposition its legacy H-Canyon neptunium to Oak Ridge National Laboratory after converting it to oxide in HB-Line. Neptunium oxide, ( $\text{NpO}_2$ ) was produced at the Savannah River Technology Center using the anticipated HB-Line flowsheet conditions. The oxide was produced from a neptunium nitrate solution via anion exchange, oxalate precipitation, and calcination at either 600 °C or 650 °C. The 98 grams of  $\text{NpO}_2$  produced in the laboratory should be representative of material produced in HB-Line and is to be used for gas generation testing to support radioactive material transportation safety analysis as part of the neptunium stabilization and disposition program at SRS. Results of each step of the oxide production will be presented.

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## INTRODUCTION

Neptunium oxide ( $\text{NpO}_2$ ) was produced on a laboratory scale for the gas generation studies needed to facilitate shipping Savannah River Site (SRS) legacy neptunium to the Y-12 facility for interim storage and eventual programmatic use at Oak Ridge National Laboratory as feed for plutonium 238 production missions. For these tests, the  $\text{NpO}_2$  produced in the laboratory needs to be uniform and representative of the HB-Line product. To make a uniform product, multiple samples of neptunium nitrate solution from H-Canyon Tank 8.5 were thoroughly combined and then divided into four large batches for production of the  $\text{NpO}_2$ . The HB-Line Phase 2  $\text{NpO}_2$  production flowsheet was emulated as closely as possible to produce a representative product in the laboratory.

The HB-Line flowsheet consists of anion exchange, oxalate precipitation, and calcination.<sup>1</sup> Unlike previously run neptunium flowsheets,<sup>2</sup> the flowsheet was optimized to favor high throughput and not efficiency and purity. At the time of this laboratory production, the proposed HB-Line flowsheet contained no wash of the anion exchange column after loading as the Tank 8.5 solution was expected to be sufficiently pure for the final product. The use of hydrazine was being considered, but had not been finalized prior to this laboratory work. The HB-Line flowsheet for oxalate precipitation specified a digestion time of five minutes at temperature and a minimal wash of the product.

Minor differences to the HB Line flowsheet exist in this experimental  $\text{NpO}_2$  production, but they are not expected to affect the product morphology of the oxide.<sup>3</sup> The conditions used in each part of this  $\text{NpO}_2$  production will be described. Where these conditions deviate significantly from the anticipated HB-Line flowsheet, an explanation as to why these deviations are anticipated to have minimal impact on oxide characteristics that are important to gas generation testing will be given. Other experimental results which will be useful for the HB Line neptunium processing will also be reported.

## EXPERIMENTAL

### Anion Exchange

A large, stainless steel shielded, ion exchange column was used for the anion exchange step. Figure 1 shows the 2.25 inch in diameter glass column filled 38cm high with Reillex HPQ resin. The bed volume of this column is one liter and the cross sectional area is  $25.6 \text{ cm}^2$ . This column has been used for previous plutonium purification. The residual plutonium was reduced from  $5.57 \times 10^6 \text{ dpm/ml}$  alpha to  $1.5 \times 10^3 \text{ dpm/ml}$  using a reductive wash. This alpha level was sufficient to prevent significant cross contamination of the neptunium product. The column was conditioned, loaded, washed and eluted in the down flow direction, due to column design. Minimal difference is expected from HB-Line, which conditions, loads, and washes its column upflow and elutes downflow. The flow rates were scaled to the HB-Line flowsheet based on cross sectional areas and the feed neptunium concentration. Based on a resin capacity of approximately 40 grams neptunium per liter of resin, two column runs were required to produce 80 grams of purified neptunium in solution.<sup>4</sup>

The column was conditioned using two bed volumes of 8 M nitric acid ( $\text{HNO}_3$ ) prior to running. The flow rate of the reconditioning wash was limited to 50 mL/minute based on the existing pump used for the column. This limitation did not create a deviation from the HB-Line baseline flow sheet for other components of the column run since lower rates are used for loading and eluting.

The neptunium feed consisted of Tank 8.5 samples collected and composited during August 2002 and January 2003. The samples were  $\sim 20\text{g/L}$  neptunium in 1.6M  $\text{HNO}_3$ . The feed acidity was adjusted to 8M  $\text{HNO}_3$  by mixing equal volumes of sample and 14.4 M  $\text{HNO}_3$ . Just prior to the column run, the neptunium valence was reduced to  $\text{Np(IV)}$  using ferrous sulfamate (FS) from a stock solution of 40% FS (2M). The FS concentration in the feed was 0.07M, based on requiring 0.03M excess reductant. Hydrazine was not needed in this experiment to prevent oxidation of the  $\text{Np(IV)}$  since the feed was prepared a short time

before column loading. If a longer time had elapsed before column feeding, hydrazine would have been added as it is in the HB-Line flowsheet. Since all of the neptunium in the experiment and HB-Line is loaded as Np(IV), not using hydrazine in the experiment will not change the final NpO<sub>2</sub> product.



Figure 1. Stainless steel shielded 1L anion exchange column.

Because the feed concentration was expected to be approximately 10 g/L neptunium, the loading flow rate was limited to match HB-Line flowsheet conditions of 14.5 mg neptunium/ min/ cm<sup>2</sup> of cross sectional area. For a 10 g/L feed, the rate at which the column should be loaded is 37 mL/min. Approximately five liters of neptunium nitrate feed were loaded on the column for each run.

No column wash was performed on the loaded neptunium in this experiment. The HB-Line flowsheet has since been changed to include pre-elution washing with 2 to 2.5 bed volumes of 8M HNO<sub>3</sub>. This will not affect the final concentration of neptunium in the anion exchange product. Not washing only increased the amount of impurities in the heart cut. The concentration of the impurities should not significantly change the morphology of the NpO<sub>2</sub> solids because particle morphology is mainly based on initial neptunium concentration, oxalate addition rate, digestion time, and temperature.<sup>5,6</sup>

The neptunium product was eluted from the anion resin using two liters of 0.17 M HNO<sub>3</sub> containing 0.05M hydrazine. Based on a HB-Line flow rate of 1.6 L/min, the scaled flow rate for elution of 37 ml/min was used. Since the anion column was not instrumented, the selection of head, heart and tail cuts was based on visual observation of the neptunium color in the eluent. The heart cut concentration was less than the 50 g/L proposed by HB-Line to prevent losses in the laboratory and to make as much NpO<sub>2</sub> as possible for the gas generation tests. To make the 50 g/L concentration, the heart cut would have to have been ended sooner which would have sent more neptunium to the tail cut. The proposed heart cut was expected to be nominally one liter of solution at 40 g/L. Following elution, two liters of 0.17 M HNO<sub>3</sub> acid were run through the column to check tailing and to put the resin in the column in low acid when not in use.

The neptunium nitrate product solutions from the two column runs were combined into a single solution prior to beginning oxalate precipitation. Mixing produced a uniform feed for the oxalate precipitation. However it extended the storage time for half this solution by four weeks. The additional Np(V) produced during the storage required an increase in the ascorbic acid concentration to 0.1M in order to reduce all the Np(V) to Np(IV). This additional ascorbic acid decreased the neptunium losses during precipitation in the laboratory. However, this small variation is not expected to impact Np oxalate crystal size or morphology and consequently is not expected to affect gas generation testing.

### Oxalate Precipitation

A neptunium oxalate (  $\text{Np}(\text{C}_2\text{O}_4)_2$  ) precipitation process similar to the elevated temperature flowsheet documented by Porter<sup>5</sup> was recommended by the Actinide Technology Section for use in Phase II of the HB-Line facility.<sup>7</sup> In the recommendation, the product from anion exchange should contain sufficient hydrazine to protect Np(IV) and ascorbic acid from oxidation by nitrous acid ( $\text{HNO}_2$ ). The feed solution, nominally 2M in  $\text{HNO}_3$ , should be heated to approximately  $50\pm 5^\circ\text{C}$  and agitated at a rate sufficient to ensure good mixing. Immediately after adjusting the solution to nominally 0.05M ascorbic acid, a sufficient volume of 0.9M oxalic acid should be added at a controlled rate over a 30 to 45 minute period to precipitate the Np(IV) and establish a 0.1M excess in the slurry. The slurry should be digested at  $50\pm 5^\circ\text{C}$ , with agitation, for 30 minutes. After cooling to ambient temperature, the precipitate should be filtered and washed with nominally five liters of 1.4M  $\text{HNO}_3$ /0.1M oxalic acid solution.



Figure 2. Equipment used for lab-scale production of  $\text{NpO}_2$ .

The proposed HB-Line conditions for oxalate precipitation are slightly different from that recommended by ATS and an attempt to closely match these HB-Line conditions with the equipment used for laboratory scale production was made.<sup>1,3</sup> The  $\text{Np}(\text{C}_2\text{O}_4)_2$  was produced on a laboratory scale using the equipment shown in Figure 2. The one liter beaker, 500 ml separatory funnel, and 500 ml stainless steel filter were chosen both for convenience and ALARA concerns. The main differences in conditions are in the final temperature prior to filtering and the method of washing the precipitate. The differences will be noted in the precipitation process used as outlined below.<sup>8</sup>

The neptunium nitrate feed solution was adjusted to 2 M in  $\text{HNO}_3$  by the addition of concentrated  $\text{HNO}_3$ . Five hundred milliliters of this solution were placed in the one liter beaker with stirring. Hydrazine was added to 0.05M, the amount expected to be present after a column run in HB-Line. The solution was heated to  $50\pm 5^\circ\text{C}$ . Immediately after attaining this temperature, 1M ascorbic acid was added to make the solution 0.1M. As noted above, this ascorbic acid concentration was larger than that proposed in the HB-Line flowsheet but the additional amount will not affect the final product. Oxalic acid at 0.9M was added from the separatory funnel slowly over 30 minutes, or at close to 10ml/min until a 0.09M excess was reached. The slurry was allowed to digest for 20 minutes at  $50^\circ\text{C}$  and cooled to  $35^\circ\text{C}$  prior to filtering. Cooling took approximately an hour. Half of the product solution was then vacuum filtered using a Millipore type FH, 0.45  $\mu\text{m}$  membrane filter. Four hundred milliliters of a 1.4 M  $\text{HNO}_3$  containing 0.1M oxalic acid wash were added to the remaining product solution. The rest of the product solution was then filtered. Minimal wash solution, ~20-30 ml, was then used to assure quantitative transfer of the

$\text{Np}(\text{C}_2\text{O}_4)_2$  from precipitation beaker to the filter apparatus. The  $\text{Np}(\text{C}_2\text{O}_4)_2$  product was then placed in a 100ml fused silica (Vycor) crucible for calcination.

Although the flowsheet temperature and digestion time are important for particle morphology the conditions in the laboratory should match those seen by the neptunium product in HB-Line. After digesting for five minutes, the large HB-Line precipitation tank will not cool appreciably from 50°C until half of the slurry is filtered. After filtering, the temperature will be lower, but is not expected to reach ambient. Cooling is much faster in a beaker; thus the 20 minute digestion in the laboratory accurately scales up the HB-Line process to produce a representative  $\text{Np}(\text{C}_2\text{O}_4)_2$  product.

The experimental filtering process accurately represents the process to be used in HB-Line. HB-Line due to removal constraints, (mainly mixing method and tank type), is going to add wash to the precipitation tank after half the slurried  $\text{Np}(\text{C}_2\text{O}_4)_2$  product is filtered. One would expect this wash method may cause  $\text{Np}(\text{C}_2\text{O}_4)_2$  particle size to change and possibly increase neptunium losses. The particle size is important to gas generation so this wash method was followed in the laboratory production. The filter pore size used in the laboratory was smaller than the HB-Line filter thus eliminating the loss of smaller particles. However, because HB-Line filter efficiency is very high once a cake is established on the filter boat, this variation in filters should not significantly change the particle size distribution in the  $\text{Np}(\text{C}_2\text{O}_4)_2$  and hence the final  $\text{NpO}_2$  product.

#### Calcination

The four  $\text{Np}(\text{C}_2\text{O}_4)_2$  precipitation products were calcined individually in small Vycor crucibles which were about three inches in diameter with a bed depth of approximately 2-3 cm. This bed depth is sufficiently shallow to allow air to permeate the powder during calcination. The HB-Line design for passing air through the powder bed during calcination may be more efficient, but should not change the  $\text{NpO}_2$  composition compared to the  $\text{NpO}_2$  made in the laboratory.

The oxalate product from each precipitation was heated to 110°C for one hour in a flow of dry air to remove any excess liquid. A dry air purge was maintained as the  $\text{Np}(\text{C}_2\text{O}_4)_2$  was heated. Two of the precipitation batches were calcined at 600°C and two at 650° C. All calcination batches were held at temperature for two hours. The muffle furnace was immediately turned off and allowed to cool to 100°C prior to removing the  $\text{NpO}_2$  product. Both the  $\text{NpO}_2$  product and  $\text{Np}(\text{C}_2\text{O}_4)_2$  are shown in Figure 3. The product was then placed in a desiccator containing color indicating Drierite desiccant (calcium sulfate) and allowed to continue to cool. Once cooled, the product was weighed and transferred to a sealed container with minimal exposure to ambient humidity in the glovebox for gas generation tests.



Figure 3. Picture of  $\text{Np}(\text{C}_2\text{O}_4)_2$  (left) in Vycor crucible before calcination to  $\text{NpO}_2$  (right).

## RESULTS &amp; DISCUSSION

## Anion Exchange

The initial feed concentration at which each of the two column runs was made was different due to the preparation of the initial tank 8.5 solution. The tank 8.5 solution arrived at the Savannah River Technology Center (SRTC) in multiple 10 ml peanut vials. Each vial was opened, added to a larger bottle, and rinsed with acid, which also was added to the feed. After some practice, less acid was used to rinse the vials which allowed a higher initial neptunium concentration to be used. The feed characterizations for both column runs are listed in Table 1 along with the final uniform solution used for precipitation.

Table 1. Feeds for column runs, and uniform feed for precipitation after being adjusted to 2M acid and 0.05M Hydrazine.

Feed	Np	HNO <sub>3</sub>	FS	Heart cut Np	Heart cut HNO <sub>3</sub>
Column run 1	7 g/L	8.0 M	0.07 M	43 g/L	0.7 M
Column run 2	~10 g/L	8.0 M	0.07 M	47 g/L	0.7 M
Mixed 1& 2	45.2 g/L	0.7 M			
Precipitation	40.6 g/L	2.0 M			

The neptunium anion exchange runs were observed closely as such large runs have not been done recently in SRTC. Initial loading of the green neptunium solution on the column produced a light grey almost shadow like section on the column. As more neptunium was introduced to the column, this section of resin increased in size and small bubbles appeared in the resin. In the second run, the loading was stopped (for replacing a feed filter) for an appreciable amount of time and the bubbles formed a larger void at the neptunium front. After all of the feed was on the column, the resin bed had swelled 10% (from 40 to 44 cm) due to the bubbles. Approximately, one third (17cm/44cm) of the resin was still available for loading. Addition of the eluting solution concentrated the Np so that it became a plug of dark forest green in color, which moved down the column. The column resin shrunk back to its original height during elution.

Sampling of the column effluent was of two types grab and bottle. All bottles of feed, loading effluents, heart cut, and tail cuts were sampled. Grab samples of the column effluent were made during both column runs. Three grab samples during loading of the neptunium feed. One prior to (head cut) and one after (tail cut) the heart cut. Results of the grab samples will not be discussed as they add minimal information.

Previous Tank 8.5 solution analysis<sup>9</sup> indicated the presence of Ag, Pb, Cr, Hg, and Se at concentrations higher than levels regulated by the Resource Conservation Recovery Act from. No mercury, above the detection limit of <0.110µg/ml by cold vapor mercury analysis(CVHG), was found in the column run feed effluent, head cut, hearts cut, and tails. The earlier Inductively Coupled Plasma-Emission Spectrometry (ICP-ES) results are suspect due to iron spectral line interferences. ICP-ES feed results from this study are listed in Table 2. Lead is not listed as its concentration was below the <3 ppm limit of detection of ICP-ES. Selenium is no longer measured by ICP-ES as it tends to give false results due to spectral line interference. Selenium is not expected to be in the feed.

The decontamination factors ( $D_f$ ) for plutonium and protactinium were measured radiochemically. No  $D_f$  was found for plutonium, as determined by alpha pulse height analysis results.  $D_f$  values calculated were between 1.0 and 1.4 but the error associated with this method may be as much as 0.4. Protactinium was found to have a  $D_f$  of 3.4 in the first column run and 3.3-3.5 in the second column run, using gamma ray analysis (after correcting for the protactinium ingrowth before counting). This value is a little higher than that predicted for two to three bed volumes of wash, but close to the three bed volume wash value of column run Cr266 determined by Kyser, which has similar conditions.<sup>10</sup>

Table 2.  $D_f$ s determined from the first column run ICP-ES results.

ICP-ES Element	Feed Solution mg/l	Heart Cut mg/l	$D_f$	2-3 bed volume wash estimate <sup>11</sup>
Ag	10.9	47.1	1.4	100
Al	41.3	109	2.3	100
Ce	132	573	1.4	-
Mo	14.5	33.1	2.7	-
Sr	6.46	16.9	2.3	-
U	151	272	3.4	2
Cd	1.9	4.61	2.5	10
Sn	17.7	52.2	2.1	-
Fe	5130	87	360	50
B	34.8	23.3	9.2	100
Ca	9.51	<2.30	>25	100
Cr	115	<0.60	>1200	100
Cu	8.78	5.03	11	100
Mg	3.18	3.44	5.7	100
Mn	26.6	0.95	170	-
Na	117	<2.20	>330	100
Ni	70.6	11.4	38	100
P	13.7	<6.9	>12	-
Si	44.4	<1.67	>160	5
Zn	10.4	1.99	32	10

The  $D_f$  values with respect to neptunium were measured with ICP-ES for the first column run. The  $D_f$  values are listed in Table 2 along with the previous two to three bed volume wash estimate. Most of the  $D_f$  values are lower than the estimates but these values would be expected to increase with washing. Silver and molybdenum are interesting in the fact that they were only detected in the feed and the heart cut suggesting washing will not increase their  $D_f$ . The other elements in the first group show some bleeding off the column via the grab samples and hence would have an increased  $D_f$  with washing.

#### Precipitation

The four precipitation runs to produce the  $\text{Np}(\text{C}_2\text{O}_4)_2$  are listed in Table 3. Two batch sizes were run and the resulting precipitates varied in weight due to the amount of time that air was pulled through the precipitate during filtration. The first and third batches had the least amount of time in the filter and hence weighed more. The first batch was wet enough to pop out of the filter as a solid cylinder. The cylinder had the volume of the neck of the filter apparatus.

Table 3. Batch precipitation and calcination results.

Batch	40.6 g/l Np	3M $\text{N}_2\text{H}_4$	1M Ascorbic	0.9M Oxalic	g Np Oxalate	Calcine Temp	g $\text{NpO}_2$
1	500 ml	8.1ml	62.5	276 ml	69.241 g	600°C	25.555
2	500 ml	8.1ml	62.5	276 ml	59.545 g	650°C	25.755
3	474 ml	7.9 ml	58.9	261 ml	69.231 g	600°C	23.900
4	474 ml	7.9 ml	58.9	261 ml	61.009 g	650°C	23.137

Neptunium losses during precipitation were greater than expected. Neptunium concentration in the filtrate was 50mg/l, as measured from the waste filtrate bottles. For a 0.09M excess oxalate solution with 1.4M HNO<sub>3</sub>, the losses would be expected to be around 10 mg/l or less at 22 °C and 50 mg/l at 45 °C.<sup>5,12</sup>

#### Calcination

After calcination each batch was found to have shrunk in volume (by approximately 30%) and to weigh between 23-25 grams. The difference in volume between the Np(C<sub>2</sub>O<sub>2</sub>)<sub>2</sub> and NpO<sub>2</sub> was appreciable as shown in Figure 3. Batch 3 was found upon mixing to contain a small iron rod. The rod was determined to be the core of a stirbar from which the Teflon had thermally decomposed during calcination. No visible difference in the NpO<sub>2</sub> was observed between this batch and the other three batches.

#### SUMMARY

Ninety eight grams of NpO<sub>2</sub> were produced for use in gas generation testing as part of the neptunium disposition program at SRS. The material was produced in large batches using the HB-Line flowsheet to be uniform and representative of material to be shipped to Y-12. The NpO<sub>2</sub> was produced from a neptunium nitrate solution via anion exchange, oxalate precipitation, and calcination at either 600 °C or 650°C. Observations and results for each of these steps are given.

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