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**Effect of Precipitation Conditions  
on the Specific Surface Area of Neptunium Oxide (U)**

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## Summary

Neptunium oxalate was precipitated under nominal and bounding HB-Line flowsheet conditions. The nominal case represents expected normal HB-Line operation. The bounding case represents process flowsheet extremes that could occur which are anticipated to decrease particle size and increase surface area. The neptunium oxalate produced under bounding conditions was used to validate the effectiveness of HB-Line calcination conditions. The maximum specific surface area (SSA) of the neptunium oxide ( $\text{NpO}_2$ ) used in gas generation testing was  $5.34 \text{ m}^2/\text{g}$  [1]. Experiments were conducted to verify that even under bounding precipitation conditions the SSA of  $\text{NpO}_2$  produced would remain within the range evaluated during gas generation testing. The neptunium oxalate from nominal and bounding precipitation conditions was calcined at  $600^\circ\text{C}$  and  $625^\circ\text{C}$ , respectively, to form  $\text{NpO}_2$ . Samples from each batch of neptunium oxalate were calcined for one, two, or four hours. Results indicate that the SSA of  $\text{NpO}_2$  continues to decrease between one and four hours. After two hours of calcination at  $625^\circ\text{C}$ , the SSA of  $\text{NpO}_2$  from the bounding case meets the surface area requirements for limiting moisture uptake.

## Background

Neptunium oxide will be produced using existing impure neptunium solutions from H-Canyon in the Savannah River Site HB-Line Phase II facility to support the future production of Pu-238 by the Department of Energy. These solutions will be purified and concentrated by anion exchange. The neptunium will be separated from the solution using an oxalate precipitation followed by filtration. The neptunium oxalate product will then be converted to  $\text{NpO}_2$  by calcining at greater than  $625^\circ\text{C}$  for a least two hours. The calcined  $\text{NpO}_2$  will then be packaged in the HB-Line Phase II facility for shipment offsite.

Because radiolysis of moisture adsorbed on  $\text{NpO}_2$  results in the production of hydrogen gas, controls are established to limit the moisture content and assure safe transportation and storage. Two important factors in the adsorption of moisture on  $\text{NpO}_2$  surfaces are relative humidity and SSA of the product. When SSA or relative humidity levels increase, the potential for adsorbing additional moisture also increases. Because the HB-Line Phase II facility has limited ability to control humidity, the emphasis for limiting moisture uptake by  $\text{NpO}_2$  is placed on controlling process parameters that affect SSA. Previous work has demonstrated that even after  $\text{NpO}_2$  with a SSA of  $5.34 \text{ m}^2/\text{g}$  is exposed to 75% relative humidity, hydrogen generation rates are acceptable for shipping [1]. Table 1 contains SSA measurements from previous experimental work [2]. In these studies, neptunium oxalate was precipitated under “nominal” conditions. The neptunium oxalate was then calcined for two hours at either  $600^\circ\text{C}$  or  $650^\circ\text{C}$  to form  $\text{NpO}_2$  [3].

There is some concern that process variations during precipitation could result in a higher SSA product. Precipitation conditions are known to affect the particle size of neptunium oxalate solids [4]; however, the SSA of  $\text{NpO}_2$  product after calcination may be relatively insensitive to precipitation conditions. The particle size of the neptunium oxalate is highly sensitive to the temperature of precipitation.

Precipitation at room temperature tends to produce fine neptunium oxalate particles that are difficult to filter. Precipitation at 50 °C followed by a digestion period produces a dense, granular product that is easy to filter, regardless of nitric acid concentration (for nitric acid concentrations between 1 and 4 M) [5]. Experimental work was performed to evaluate the effect of precipitation conditions on the SSA of the  $\text{NpO}_2$  product.

**Table 1: Np SSA measurements from previous studies ( $\text{m}^2/\text{g}$ )**

Calcination Temperature* (°C)	SSA ( $\text{m}^2/\text{g}$ )	Precision ( $1\sigma$ ) (%)	Reference
600	5.34	0.6	2
650	3.68	1.0	2
650	3.67	1.9	2

\* All samples calcined for 2 hours.

The scope of these experiments was limited to nominal and bounding conditions and not designed as a full parametric study. In the nominal case, precipitation conditions similar to the HB-Line flowsheet were chosen. In the bounding case, precipitation conditions were chosen that are expected to maximize SSA. The nominal case serves as our experimental control with the expectation that SSA will be similar to previous measurements. The bounding case is used to demonstrate the efficacy of calcinations at 625 °C. In other words, “if all the precipitation conditions are as far from nominal in the direction that should produce the smallest particle size (and probably the largest SSA if a spherical model holds) as allowed by HB-Line controls, would calcination at 625 °C produce a SSA less than or equal to the  $\text{NpO}_2$  evaluated in gas generation testing?”

## Experimental

### Ion Exchange

Neptunium solutions from H-Canyon were purified and concentrated using anion exchange by E. A. Kyser [6]. The combined product solution of three anion exchange runs was 59 grams per liter neptunium, 1.3 M nitric acid, and approximately 0.05 M hydrazine.

### Precipitation - Nominal Case

Neptunium oxalate solids were precipitated using methods similar to those described by Bronikowski [3] and similar to the HB-Line flowsheet. Table 2 contains a summary of precipitation conditions. The neptunium feed solution (containing 6.0 grams of neptunium) from ion exchange was adjusted to 4.0 M nitric acid (higher than the 2.0 M nitric acid solution used by Bronikowski). The feed solution was heated to 50 °C using a ceramic top hotplate. The hotplate has an electronic temperature controller

linked to an immersion type K thermocouple to allow temperature control based on the temperature of the solution. The solution was made 0.10 M in ascorbic acid. The addition of ascorbic acid was required to reduce any neptunium(V) to neptunium(IV). Immediately after the ascorbic acid addition, 0.90 M oxalic acid was pumped into the solution at a constant rate (approximately 2.7 ml/min). The temperature was maintained at  $50\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$  during the oxalic acid addition. A stir bar was used to stir the solution at a moderate rate (250 RPM) during the addition. The oxalic acid addition took approximately 31 minutes. After the addition, the solution was maintained at  $50\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$  for 20 minutes with stirring. The solution was allowed to cool to  $35\text{ }^{\circ}\text{C}$  over approximately one hour. Once the solution reached  $35\text{ }^{\circ}\text{C}$ , it was then filtered using a  $0.45\text{-}\mu\text{m}$  filter and a filter flask with vacuum. The solution filtered very quickly. A small amount of rinse solution (1.5 M nitric acid and 0.10 M oxalic acid) was used to remove any remaining solids from the beaker. Air was passed through the filter cake for 30 minutes for drying. The filter cake appeared to dry very uniformly and did not crack. The neptunium solids were left on the filter overnight to dry.

**Table 2: Precipitation conditions**

Case	Nitric acid concentration (M)	Precipitation temperature ( $^{\circ}\text{C}$ )	Mixing	Precipitation time (minutes)
Nominal	4.0	50	Moderate (250 RPM)	31
Bounding	1.5	35	Vigorous (400 RPM)	17

An attempt was made to match HB-Line precipitation conditions in the laboratory; however, some deviations from the HB-Line precipitation method were required. These differences are not expected to have a significant impact on the SSA of  $\text{NpO}_2$ . It should be noted that the focus of this study was to evaluate the sensitivity of  $\text{NpO}_2$  SSA to precipitation conditions, not to duplicate HB-Line precipitation conditions. For example, the HB-Line flowsheet does not include neptunium valence adjustment with ascorbic acid, but valence adjustment is used in the experimental work because of the lag time between anion exchange and precipitation. The filter pore size used in the laboratory is significantly smaller than pore size of HB-Line filters. Using a smaller filter pore size is conservative since it prevents the loss of smaller particles. These test conditions have been maintained consistent with earlier  $\text{NpO}_2$  production [3].

Another variation between process and laboratory methods is intended to adjust for the rate of filtration and solution cooling. In laboratory experiments, the solution was digested for 20 minutes and then cooled to  $35\text{ }^{\circ}\text{C}$  prior to filtration. This longer digestion and cooling was used because the laboratory filtration is complete within a few minutes. In HB-Line, filtering of the solution starts after a 5-minute digestion period; however, the filtration process takes much longer to complete resulting in additional



digestion time. A rinse solution is added to the precipitator during the filtration process. The addition of the rinse solution, combined with heat losses during the transfer of solution to the filter, cools the solution before it reaches the HB-Line filter. More details of variations between laboratory and plant conditions are discussed in an earlier report [3].

### Precipitation - Bounding Case

In the bounding case, precipitation conditions were chosen to maximize surface area by minimizing particle size. Table 2 contains a summary of the precipitation conditions for the bounding case. The neptunium feed solution (containing 6.0 grams of neptunium) was adjusted to 1.5 M in nitric acid. The feed solution was then heated to 50 °C and made 0.10 M in ascorbic acid. The solution was maintained at 50 °C  $\pm$  5 °C for 15 minutes then allowed to cool to 35 °C. It was necessary to heat the solution to 50 °C to ensure that the ascorbic acid reduced any neptunium(V) to neptunium(IV). The reaction of ascorbic acid with neptunium(V) is very slow at lower temperatures and nitric acid concentrations [6]. Once the solution reached 35 °C, the stirring was increased to a vigorous rate (400 RPM) and oxalic acid was pumped into the solution at a rate of approximately 5.2 ml/min. The temperature was maintained at 35 °C  $\pm$  5 °C during the addition. Due to difficulties with the pump, flow was stopped for approximately three minutes about seven minutes into the addition. The remaining oxalic acid was added using a slurry pipette. The total addition time was 17 minutes, which was slightly greater than the target addition time of 15 minutes. Immediately after all of the oxalic acid was added, the solution was filtered using a 0.45- $\mu$ m filter. The filtration took much longer than the filtration for the nominal case, which suggests the neptunium oxalate particles were significantly smaller than for the nominal case. The filter cake was dried for about 40 minutes by passing air through the cake. The filter cake cracked during drying and did not appear to dry evenly. The neptunium oxalate solids were left on the filter overnight to dry.

### Calcination – Nominal Case

The neptunium oxalate product from the nominal precipitation case was divided into three roughly equal samples. Each sample was placed in a 30-ml high-form crucible. Each sample contained approximately two grams of neptunium. All three samples were placed in a Thermolyne Model 1300 furnace and dried at approximately 110 °C for one hour. The temperature of the furnace was then increased to 600 °C. Once the furnace reached 600 °C, one crucible was removed after one hour. A second crucible was removed after two hours and the last crucible was removed after four hours. Temperatures were based on the oven thermocouple reading.

### Calcination – Bounding Case

The neptunium oxalate product from the bounding precipitation case was divided into three roughly equal samples. Each sample was placed in a crucible. Each sample contained approximately two grams of neptunium. The solids were much damper and more difficult to handle than the solids for the nominal case despite being allowed to dry longer. The weight of the damp solids was 30% higher than that of the nominal case even though approximately the same amount of neptunium oxalate was present for both cases. All three samples were placed in the furnace and dried at approximately 110 °C for one

hour. The temperature of the furnace was then increased to 625 °C. Once the furnace reached 625 °C, one crucible was removed after one hour. A second crucible was removed after two hours and the last crucible was removed after four hours.

### Measurement of SSA

Samples of  $\text{NpO}_2$  were taken from each crucible. The SSA of each sample was measured using the BET (Brunauer, Emmet, and Teller) isotherm method. A Micromeritics Gemini 2360 surface area analyzer and Flowprep 060 de-gassing unit were used in the surface area analysis. A glass standard with a surface area of  $5.0 \pm 0.3 \text{ m}^2/\text{g}$  was also analyzed. This instrument and method were used for SSA measurements associated with  $\text{NpO}_2$  gas generation testing [2]. Based on previous measurements of  $\text{NpO}_2$  SSA, the method precision has a 95% confidence interval of  $\pm 2.2\%$  [7].

### Scanning Electron Microscopy (SEM)

SEM images were taken of neptunium oxalate and of  $\text{NpO}_2$  (calcined for four hours) from both the nominal and the bounding case to obtain qualitative estimates of particle size. With the exception of the neptunium oxalate sample for the nominal case, the samples for SEM analysis were prepared by dusting a few milligrams of material onto an adhesive sample plate. The neptunium oxalate sample for the nominal case was prepared by attaching a small piece of the filter paper that was used to filter the neptunium oxalate after precipitation to the sample plate. This procedure was done because the nominal case sample had already been calcined when the decision was made to submit samples for SEM analysis.

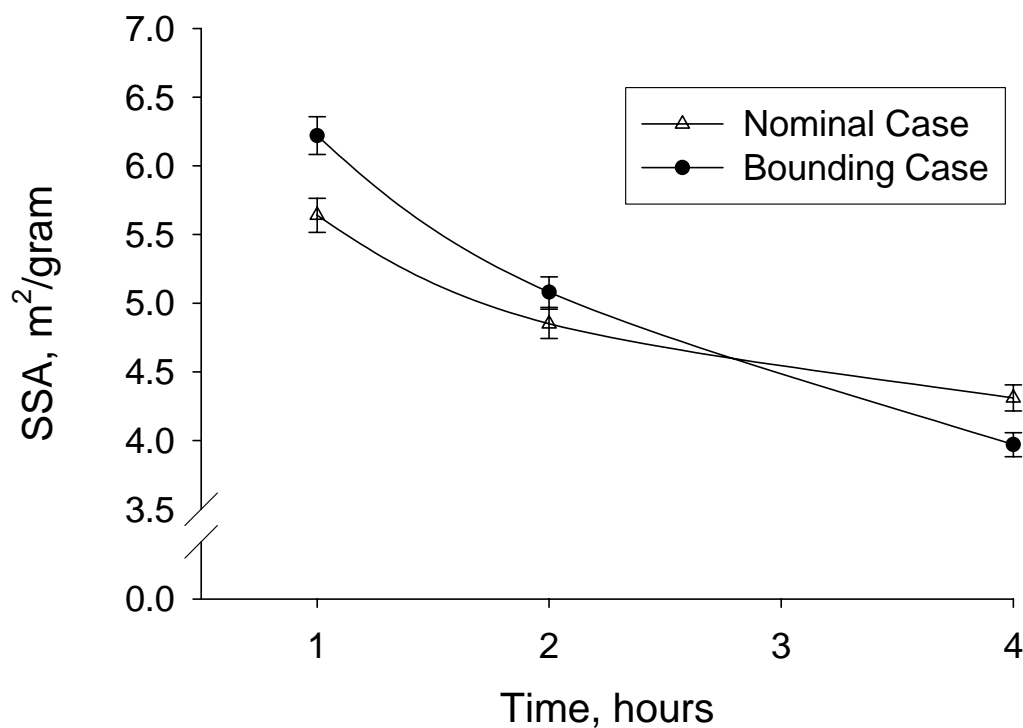
## **Results and Discussion**

SEM images of neptunium oxalate and  $\text{NpO}_2$  from both the nominal and the bounding case are contained in Appendix 1. The SEM image of neptunium oxalate from the nominal precipitation is likely not representative of bulk oxalate due to the method of sample preparation. The SEM images of  $\text{NpO}_2$  show qualitatively that the  $\text{NpO}_2$  (calcined for four hours) particles are much larger for the nominal case than for the bounding case. Table 3 contains the results of the SSA measurements of  $\text{NpO}_2$  for both the nominal and bounding conditions. The values from Table 3 with error bars are plotted versus calcination time in Figure 1. The SSA for the bounding case is higher than the SSA for the nominal case after one hour of calcining. For both bounding and nominal conditions, the SSA decreases significantly between one and four hours. The shape of the curves in Figure 1 suggests that calcining  $\text{NpO}_2$  longer than four hours would continue to reduce the SSA under both bounding and nominal conditions.

**Table 3: SSA measurement results (m<sup>2</sup>/g)\***

Case	Calcination temperature (°C)	1 hour	2 hours	4 hours	Standard (5.0 ± 0.3 m <sup>2</sup> /g)
Nominal	600	5.64	4.85	4.31	4.96
Bounding	625	6.22	5.08	3.97	4.87

\* The 95% confidence interval of the method precision is ± 2.2% [7].

**Figure 1. Graph of SSA versus calcination time for nominal and bounding case**

The rate of decrease in SSA between one and four hours is greater for the bounding case than for the nominal case. After one hour of calcination, the SSA of the bounding oxide is significantly greater than that of the nominal oxide. This result is not surprising since the bounding precipitation conditions are expected to produce smaller particles. After two hours, the SSA of the bounding oxide is only slightly greater than that of the nominal oxide and after four hours of calcination, the SSA of the bounding case oxide is actually lower than that of the nominal case. One factor that likely has a major contribution to

the difference in rate of change in SSA is the calcination temperature. The bounding case oxide was calcined at 625 °C while the nominal case oxide was calcined at 600 °C. Previous work has shown significant differences in SSA for  $\text{NpO}_2$  calcined at 600 °C and 650 °C for two hours (5.34  $\text{m}^2/\text{g}$  and 3.68  $\text{m}^2/\text{g}$ , respectively) [2]. With limited data available, it is difficult to quantify the effect of calcination temperature on the rate of SSA reduction. Other factors, such as particle size, may also affect the rate of decrease in SSA during calcination.

The  $\text{NpO}_2$  sample from the nominal case that was calcined for two hours can be compared to the historical data. Neptunium oxide in a previous study that was created under similar precipitation and calcination conditions had a SSA of 5.34  $\text{m}^2/\text{g}$  [2, 3]. This value is slightly higher than the SSA of 4.85  $\text{m}^2/\text{g}$  that was measured in this study. A variety of factors may have contributed to this difference in SSA. One difference in precipitation conditions is that 2 M nitric acid was used in the previous study while 4 M nitric acid was used in this study. Other differences in precipitation conditions include batch size, neptunium concentrations, and oxalic acid addition rate. These results demonstrate that differences in precipitation conditions can lead to changes in SSA of the  $\text{NpO}_2$  product.

Assuming smooth spherical particles, a theoretical SSA for  $\text{NpO}_2$  can be calculated. For  $\text{NpO}_2$  particles that are 1 and 30  $\mu\text{m}$  in diameter, the theoretical SSA would be 0.54 and 0.018  $\text{m}^2/\text{g}$ , respectively. The large difference between these theoretical values and the measured values illustrates the importance of surface roughness and porosity to the SSA. This comparison shows that a spherical model of surface does not fit the particular case. Although SSA after one or two hours of calcination is greater for the smaller particle size, the large difference in particle size does not yield a similar difference in SSA.

After two hours of calcination, both the nominal and the bounding oxides have a SSA less than 5.34  $\text{m}^2/\text{g}$ , which is less than the maximum SSA evaluated in gas generation testing [1]. Based on these results, calcination at greater than 625 °C for at least two hours will provide acceptable SSA (less than 5.34  $\text{m}^2/\text{g}$ ) under the precipitation conditions evaluated in this study. These results address concerns associated with chemistry variations during precipitation. The evaluation of scale-up effects is beyond the scope of this study.

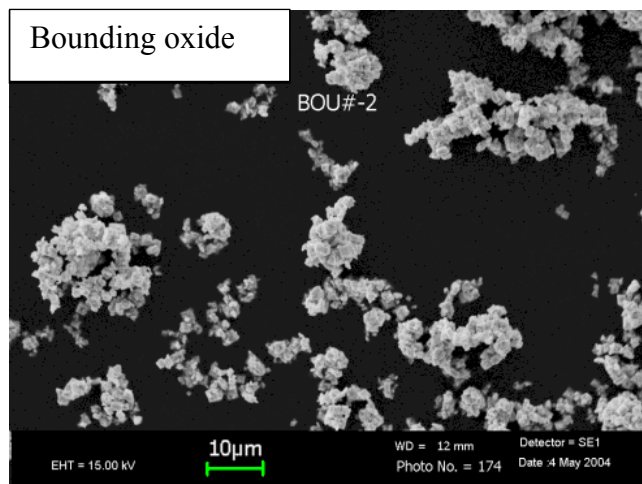
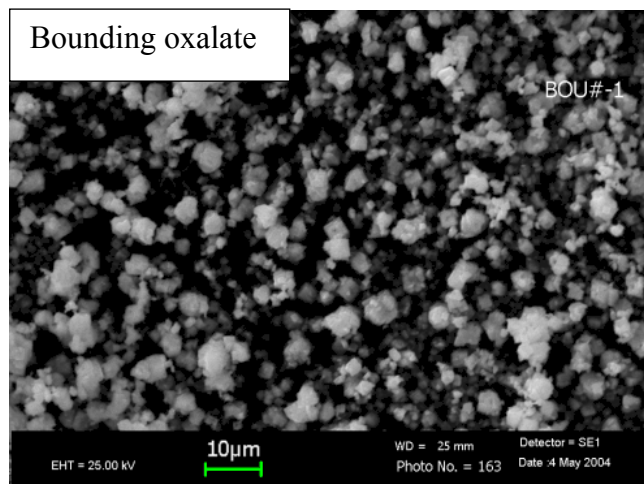
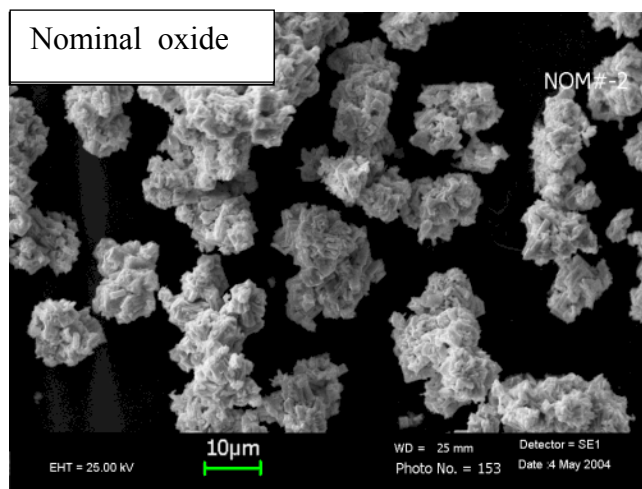
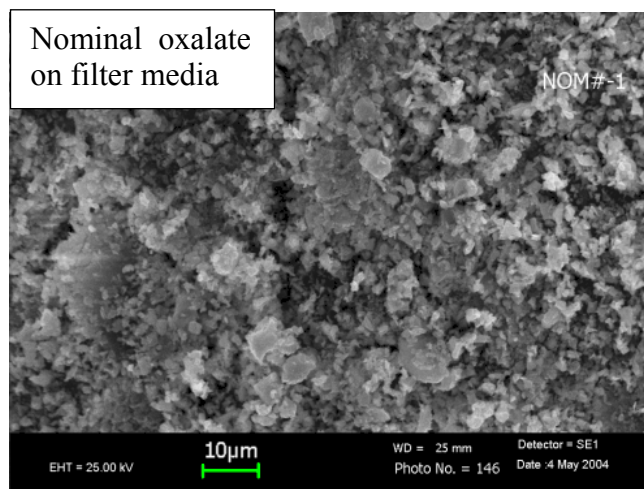
## Conclusions

Many factors have a significant effect on the SSA of the  $\text{NpO}_2$  product. These factors include precipitation conditions, calcination temperature, and calcination time. Even though poor precipitation conditions which result in the formation of smaller particles may tend to increase the SSA of the product, calcining neptunium oxalate precipitated under these bounding conditions at 625 °C for two hours produced  $\text{NpO}_2$  with a SSA of 5.08  $\text{m}^2/\text{g}$ . This SSA is acceptable based on material used in gas generation testing [1]. The results also indicate that calcining for four hours will further reduce the SSA of  $\text{NpO}_2$ .

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## Appendix 1 – SEM Images



All SEM images are at approximately 1000X magnification