

Neptunium Oxide Processing

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ABSTRACT

The Savannah River Site's HB-Line Facility completed a campaign in which fifty nine cans of neptunium oxide were produced and shipped to the Idaho National Laboratory in the 9975 shipping container. The neptunium campaign was divided into two parts: Part 1 which consisted of oxide made from H-Canyon neptunium solution which did not require any processing prior to conversion into an oxide, and Part 2 which consisted of oxide made from additional H-Canyon neptunium solutions which required processing to purify the solution prior to conversion into an oxide. The neptunium was received as a nitrate solution and converted to oxide through ion-exchange column extraction, precipitation, and calcination. Numerous processing challenges were encountered in order to make a final neptunium oxide product that could be shipped in a 9975 shipping container. Among the challenges overcome was the issue of scale: translating lab scale production into full facility production. The balance between processing efficiency and product quality assurance was addressed during this campaign. Lessons learned from these challenges are applicable to other processing projects.

INTRODUCTION

Neptunium-237 oxide is used for the production of plutonium-238 to support NASA space missions. Previous chemical processing at the Savannah River Site (SRS) H-Canyon Facility during the 1970s and 1980s produced neptunium solution. This solution was stored in an H-Canyon tank until 2003 when the decision was made to stabilize the solution into neptunium-237 oxide to support future plutonium-238 production. Processing the solution into neptunium oxide was performed in the HB-Line Facility at SRS.

DISCUSSION

Production Process

The HB-Line facility was used to concentrate, purify and convert neptunium nitrate solution to neptunium oxide powder. The H-Canyon feed material was transferred to the HB-Line facility at approximately 13 g/L neptunium. After receipt of each batch of neptunium nitrate solution into HB-Line, the solution was mixed and sampled to ensure material accountability. The feed solution contained neptunium at +4, +5, and +6 valence states. Ferrous sulfamate was added to the feed material to ensure the valence was adjusted to +4. Additionally, hydrazine mononitrate was added to restrict the ability of the neptunium to oxidize from +4 back to +5. Maintaining the +4 valence state ensured efficiency of the precipitation and filtration processes which occurred after column operations. Prior to transfer to the anion-exchange resin column, nitric acid was added to maintain the appropriate molarity for column operations. Approximately 2000 g of neptunium was loaded on the anion column per batch. The neptunium

solution was loaded onto the column, washed to remove impurities, and eluted from the column. This process succeeded in stripping most of the impurities from the solution and concentrating the neptunium. The concentration after the anion exchange process was approximately 50 g/L neptunium. The neptunium nitrate was then heated and transferred to a precipitator. Oxalic acid was added to the neptunium solution in a direct strike precipitation process. The precipitant was collected on a screen in a “filter boat” where the liquid is removed from the neptunium oxalate in a process known as filtration. The neptunium oxalate precipitant was then calcined in a furnace to form neptunium oxide powder. The oxalate was heated above 635°C for at least 3 hours to form approximately 1200 g of neptunium oxide per filter boat. The neptunium oxide was packaged in sealed product cans, with approximately 6 kg neptunium per can, which were loaded into a 9975 shipping container for shipment from SRS to Idaho National Laboratory (INL). Prior to shipment to INL, the 9975 shipping containers loaded with neptunium oxide were transferred from HB-Line to an onsite storage location for interim storage.

In order to provide input to transportation requirements, prototypical samples of neptunium oxide were created using the process flowsheet. Multiple samples of the neptunium nitrate solution were combined and divided into four large batches for lab-scale production of neptunium oxide. The lab scale production followed, as closely as possible, the anticipated HB-Line flowsheet. Minor differences were not expected to affect product morphology of the oxide. Based on the lab-scale production and subsequent gas generation testing, it was determined that calcining the neptunium oxalate for a minimum of two hours at 625°C would sufficiently convert the oxalate to oxide to limit the moisture in the final product. Limiting moisture is critical for shipping and storage due to the potential for the build-up of hydrogen. Lab scale production also indicated the amount of impurity removal that could be expected from the anion-exchange process. Based on these results, neptunium oxide moisture and product impurity limits were specified for transportation purposes.

The decision was made to test the first batches of actual oxide product extensively for neptunium concentration. This verified that losses were minimized and the product was relatively pure. No attempt was made to validate the amount of anticipated moisture or expected low level impurity values due to the prior facility experience with this type of process for the production of plutonium.

Moisture Concern

During the production of neptunium, the HB-Line facility tracked the amount of neptunium to ensure material accountability. As part of a material accountability check, a mass balance was performed on material samples. Initial samples indicated that some cans may have potentially high moisture contents. Based on additional sampling of material and an in-depth process history review, four cans were identified as potentially having high moisture. After investigation, only one of the four was confirmed as an outlier. High moisture content brought into question the material’s compliance with the regulatory shipping documents. These high weight loss results associated with excess moisture indicated that there may be incomplete calcination of the neptunium oxide product, which brought into question the ability of HB-Line to rely solely on calcination temperature and time as process controls for neptunium oxide moisture content.

Based on the in-depth process history review, several potential indicators were identified that would contribute to high moisture levels in the final oxide product. During the calcination of the neptunium oxalate, a furnace off-gas system was used to remove the water from the material as it was heated. For the one can with confirmed high moisture content, lower airflow during the calcination process and significant moisture in the off-gas system was identified. At the time of processing these conditions were reported. The importance of these indicators was not known or understood at the time, since they were not important for lab scale production. In addition, these factors were not as important for previous plutonium production and, based on the reliance on prior processing knowledge, were thought not to be critical for neptunium production. As a result, these were not identified as potential scale-up issues. The time that the oxalate took to reach the final temperature was also higher for the one outlier material. In addition, a correlation was identified with the inclusion of sweeping material and higher moisture content.

Based on the key metrics identified from the process history review, additional process quality steps were added into the production process. This included steps to ensure an appropriate air dry of the neptunium oxalate prior to calcinations. Steps were also added to verify adequate purge flow during calcinations. These steps helped to ensure that all of the excess moisture was removed from the system and transported away from the oxide product. Additional reviews were made of the temperature curves during the calcinations to verify that the oxalate was getting to the appropriate temperature and to identify any process abnormalities. These steps were added to reduce the possibility of having high moisture in the final product. Additional moisture testing, as well as periodic full impurity testing, was used to validate the process changes. The decision was made to isolate sweepings (oxide that is spilled) and not add it to the product stream. An additional change was made to the sampling technique. Prior sampling assumed all of the oxide was homogeneous and samples were pulled from the top of each can. The revised sampling plan involved mixing a small amount of oxide from each batch and sampling from the mixture. Moisture sample results were also reviewed prior to being transferred from HB-Line to an the onsite storage location. As a final step, the operation logbooks were reviewed to identify any other process abnormalities that could affect the final product quality.

The intent of these changes was to ensure that no cans would have high moisture content. Possible impact to overall product quality was also addressed.

The four cans with suspect moisture values were returned to HB-Line facility from the onsite storage location for rework. The material in the cans were recalced and then repackaged. Sample results after the rework showed that the moisture content was well within acceptable limits. Based on a mass loss study, only one of the cans was confirmed to have excess moisture prior to rework.

Impurity Concern

While HB-Line was implementing process controls on the neptunium oxide Part 1 product, additional H-Canyon solutions were under consideration for future processing, Part 2 material. One of these solutions was a drop tank from the HB-Line neptunium process. Sample results showed the plutonium isotopic distribution was different than the original H-Canyon solution distribution. The original solution was high in plutonium-238 while the drop tank being

evaluated was high in plutonium-239. Neptunium oxide sample results from the most recent product cans at the time showed the plutonium limits within the 9975 SARP (Safety Analysis Report for Packaging) content table limits of ≤ 611 ppm total plutonium, ≤ 500 ppm plutonium-238, ≤ 88 ppm plutonium-239. However, sampling from some of the first neptunium oxide product cans revealed five cans with plutonium-239 concentrations greater than 88 ppm, although total plutonium was less than the 611 ppm limit.

In addition to the variation in plutonium isotopic concentration, some of the non-radioactive impurities associated with the neptunium oxide product were higher than expected and above the 9975 SARP content table limits. After investigation, it was determined that the main reason for this was the addition of spilled oxide back into the product can. In addition, it was determined that sufficient margin did not exist with respect to the limits for specific element impurities as identified in the SARP.

The processing area in HB-Line used for neptunium production was previously used for production of plutonium-239 oxide. Prior to the start of the neptunium oxide campaign; a flush program was conducted to remove residual amounts of plutonium in the processing tanks, gloveboxes, and vessels. This program verified sample results from the processing tanks to ensure that the level of plutonium was minimal. The plan also included provisions for wiping down glovebox cabinets and calcinations equipment. Although the cabinets were wiped down, no quantitative validation was performed for this area. Sample scoops, vials, glove, and filter boats were replaced and waste was removed from the mechanical line processing area.

Based on the higher plutonium-239 concentration than expected, it is likely that some residual plutonium was left in the glovebox cabinets. This residual plutonium made its way into the product can through the practice of adding spilled oxide back into the product can. This routine was stopped after the corrective action for high moisture. Additional sampling was put into place to verify that the plutonium isotopics and total plutonium were acceptable, as well as uranium and neptunium assay.

Additional Material

The Part 1 neptunium campaign concluded with fifty cans produced (at approximately 6 kg per can). Due to the success of this initial campaign, additional neptunium solution was identified for further processing as Part 2. This Part 2 material contained a higher amount of impurities than the original solution. It was determined that the HB-Line anion-exchange column would not be able to remove all of the impurities to meet the existing neptunium oxide product quality requirements for the 9975 package. In addition, some of these impurities, such as iron, would adversely affect the process flowsheet. The decision was made to process the material through two separate solvent extraction processes in the H-Canyon facility prior to transferring the material to the HB-Line facility.

The initial solvent extraction was designed to remove the sulfates from the neptunium solution. The second extraction step was designed to remove plutonium and cerium, as well as other impurities. Combined, the two extraction steps were intended to make the solution at least as pure as the original neptunium solution, with the exception of uranium. Uranium would follow the neptunium through the H-Canyon process and would have to be addressed in HB-

Line. After completion of the solvent extraction steps, sample results confirmed that the process behaved as expected.

After receipt of the newly purified neptunium solution, the only change from the original process was the addition of more washing steps for the anion-exchange column. Based on prior experience, it was known that the amount of uranium versus neptunium was reduced for each wash. By adding more washes, the high level of uranium was reduced to acceptable levels. The additional lessons learned from the moisture and impurity concerns were carried over to this new production batch. Nine additional cans of neptunium were produced from this second batch of material.

CONCLUSION

A total of fifty-nine cans of neptunium oxide were produced in the HB-Line facility and shipped to Idaho National Laboratory. While the campaign as a whole was successful, several lessons learned were identified as part of the process. These factors included the investigation of potential scale-up issues when proceeding from lab-scale to facility-scale production. Another key point is the need to track key leading indicators and periodically validate product quality through testing. Although these additional activities take time and can slow production, finding the proper balance is critical to prevent rework, which creates even longer delays.