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PACKAGING AND TRANSPORTATION OF NEPTUNIUM OXIDE

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ABSTRACT

The Savannah River Site's HB-Line Facility completed a campaign in which fifty (50) cans of neptunium oxide were produced and shipped to the Idaho National Laboratory in the 9975 shipping container. This shipping campaign involved the addition of neptunium oxide to the 9975 Safety Analysis Report for Packaging (SARP) as a new content and subsequently a Letter of Amendment to the SARP content table. This paper will address the proper steps which should be taken to add a new content table to a SARP. It will also address the importance of product sampling and understanding the material shipping requirements of a SARP.

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 a 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 would be performed in the HB-Line Facility at SRS.

The HB-Line Facility completed a campaign in which fifty (50) cans of neptunium oxide was produced and shipped to the Idaho National Laboratory (INL) in the 9975 shipping container. The shipping campaign involved the addition of neptunium oxide to the Model 9975 B(M)F-85 Safety Analysis Report for Packaging (9975 SARP) as a new content and then a Letter of Amendment to the 9975 SARP content table. This paper will address the proper steps which should be taken to add a new content table to a SARP. It will also address the importance of product sampling and understanding the material shipment requirements of a SARP.

Neptunium nitrate solution from the H-Canyon Facility was transferred to the HB-Line Facility were it was concentrated, purified, and then converted to an oxide powder. The H-Canyon feed material was approximately 13 g/l neptunium. Ferrous sulfamate was added to the neptunium feed to ensure the neptunium valence was adjusted to +4. After adjusting the molarity, the solution was transferred to an anion-exchange resin column. Approximately 2000 g of neptunium was loaded on the anion column per batch. The anion exchange concentrated and purified the neptunium nitrate solution to 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”. The neptunium oxalate precipitant was calcined in a furnace to form neptunium oxide powder. The oxalate was heated above 635ºC for 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 INL

The final neptunium oxide product is not nearly as hazardous as plutonium oxide because it has minimal heat generation and a very large critical mass limit. However, it does decay to protactinium-233 which has an energized gamma that requires shielding. There was essentially no information regarding potential hydrogen gas generation from low-fired (approximately 600ºC) neptunium-237 oxide. Since shielding requirements can be readily determined, the only safety issue requiring additional study and evaluation is the potential for hydrogen generation.

HYDROGEN GENERATION

Gas generation testing of plutonium oxide has shown that specific surface area (SSA) and moisture content are two important factors in hydrogen (and oxygen) gas generation of plutonium oxide. For plutonium oxide, SSA and moisture uptake decrease with increasing temperature used to calcine the material. Neptunium oxide was expected to behave similarly.

Prior to commencement of neptunium processing, a liquid sample of H-Canyon neptunium solution was converted to neptunium oxide at the Savannah River National Laboratory (SRNL) to determine the neptunium oxide hydrogen gas generation rates and provide input to the 9975 SARP content table. The neptunium oxide was produced according to the anticipated HB-Line flowsheet (process) consisting of anion exchange, oxalate precipitation, filtration, and calcination. Characterization of the neptunium oxide product to be used in gas generation tests included bulk and tap density measurements, X-ray diffraction, particle size distribution, specific surface area measurements, and moisture analysis. Temperatures of 600ºC and 650ºC were chosen to calcine the neptunium oxalate based on the expected HB-Line furnace operating temperature of 625ºC +/- 25ºC. Additionally, a one time sample of the neptunium oxide produced by SRNL was analyzed for chemical element characteristics. The SRNL produced neptunium oxide was considered to be uniform and representative of the oxide to be produced in HB-Line.

The SRNL neptunium oxide demonstrated that the HB-Line flowsheet (process) would remove most of the radioactive and non-radioactive impurities from the feed solution except for thorium. Thorium, as expected, tracked through the HB-Line processing along with the neptunium and converted to thorium oxide. Gas generation testing determined the thorium oxide had negligible effect on the oxide products characteristics. A similar solution cleanup phenomenon was seen previously by HB-Line during a recent plutonium oxide campaign.

In general the H-Canyon neptunium solution was considered very pure. Sample results from the neptunium solution showed approximately 1 – 2 % thorium, low levels of plutonium ($\leq$ 611 ppm total Pu, $\leq$ 500 ppm Pu-238), very low levels of uranium (< 50 ppm), and low levels of non-radioactive elements.

The SRNL neptunium oxide results indicated that the neptunium oxide would be purer than the original H-Canyon solution. Thus the impurities and their concentrations in the H-Canyon solution were submitted for inclusion into the 9975 SARP content table revision as potential neptunium oxide impurities. The 9975 SARP content table limits on neptunium oxide had the exact plutonium isotopic distribution, uranium isotopic distribution, and non-radioactive element distribution as the original feed solution. No margin was given for processing variability or sample measurement uncertainty.

The HB-Line Facility implemented the SRNL neptunium process recommendations. The facility process areas, equipment, and piping were cleaned to remove any material that would contaminate the neptunium oxide product. The thoroughness of this cleaning was not validated in all process areas. Limited sampling was initiated, but full characterization sample analysis of the final product was not performed. Once the neptunium oxide product was made, SRS shipped it to INL per the 9975 SARP citing the limited sampling and process knowledge that the material met the specified content table criteria.

NEPTUNIUM OXIDE PRODUCT DEVIATIONS

Two events occurred during the neptunium oxide campaign that demonstrated the HB-Line assumptions used to show SARP compliance were flawed. The first event involved discrepancies in material balances being conducted for nuclear material accountability purposes. After several months of investigation, higher than assumed moisture amounts in the final neptunium oxide product was suspected as the culprit. Actual sampling of material revealed four cans with potential high moisture, of which one actual outlier was identified. It should be noted that the 9975 SARP did not specify a specific moisture limit, but stated the material must be prepared in accordance with the SRNL neptunium oxide method which limits the moisture content of the material. According to the SRNL report material processed per the HB-Line flowsheet and calcined at approximately 625ºC should not have a weight loss in excess of 0.3 wt%. 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. Additional controls and post processing reviews were implemented to verify the material was adequately calcined.

While HB-Line was implementing moisture controls on the neptunium oxide product, additional H-Canyon solutions were under consideration for future processing. One of these solutions was a drop tank from the HB-Line neptunium process. Sample results showed the plutonium isotopic distribution 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 SARP 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 Pu 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.

Both of these incidents were reportable transportation incidents resulting in SRS suspending 9975 shipments of neptunium oxide. To resume shipments, a Letter of Amendment to the 9975 SARP had to be written by SRS and approved by DOE EM-60.

REVISED NEPTUNIUM OXIDE CONTENT

The purpose of the Letter of Amendment to the 9975 SARP was to establish neptunium content criteria which would be safe to ship in a 9975 shipping container and could be achieved by the HB-Line Facility. The approved 9975 content table for neptunium oxide as it existed in the 9975 SARP was based more on the H-Canyon feed tank sample results rather than the amounts of radioactive and non-radioactive material that was safe to ship in the 9975. The process for writing the Letter of Amendment had to focus on determining what parameters were important for safe shipment while staying within the bounds of the original gas generation testing.

The 9975 SARP content table for neptunium oxide had three major issues. First, no specific moisture limit was listed - leaving compliance up to interpretation with no measuring stick to compare to. Second, the plutonium isotopic distribution exactly matched the original feed solution isotopic distribution – leaving no margin for process variability or process upsets. Even though the facility process did remove some plutonium it contaminated the neptunium oxide product with a different plutonium isotopic distribution. Third, the non-radioactive elemental limits were set too low – laboratory analytical measurement uncertainly and process variability were not considered when the impurity limits were agreed upon. The only potential safety issue with the non-compliant levels of specific plutonium isotopes and non-radioactive impurities was the impact on hydrogen gas generation. The levels of these non-compliant constituents was quite small (ppm order of magnitude) and, thus, their impact was negligible.

Since additional gas generation testing was not feasible, the letter of amendment safety basis had to stay within the bounds of the previous testing. The primary parameters associated with gas generation of the neptunium oxide product are moisture content and total alpha dose (or activity). Nearly all of the decay energy associated with the neptunium oxide product is a result of alpha decay. In the gas generation testing approximately 92.1% of the total alpha activity came from plutonium isotopes, of which approximately 99.9% was due to plutonium-238. Approximately 7.6% of the total alpha activity came from neptunium-237, and together plutonium-238 and neptunium-237 accounted for greater than 99.5% of the total alpha activity in the tested oxide. Because the neptunium-237 alpha activity remained essentially constant, if the plutonium-238 content and total plutonium content met the original SARP limits of 500 ppm and 611 ppm then the total alpha activity (dose) of the neptunium product would be bounded, within the experimental uncertainly, by the SRNL gas generation testing. As for moisture, the SRNL report stated material processed per the HB-Line flowsheet and calcined at approximately 625ºC should not have a weight loss in excess of 0.3 wt% (also referred to as loss on ignition – LOI). Based upon the SRNL LOI measurement control chart, LOI measurements between 0.10 wt% and 0.23 wt% were determined to be acceptable.

A quantitative determination of how impurities impact gas generation was not possible without additional gas generation testing. However the available measurement data from the neptunium oxide product indicated that the total impurities were present at significantly less than 1% of the sample mass. After taking into consideration the uncertainty associated with small quantities of light element impurities, the major factors driving the hydrogen gas generation rate of this neptunium oxide continue to be radiation does rate and moisture content.

The neptunium oxide Letter of Amendment to the 9975 SARP included new content limits for neptunium oxide such as specifying a moisture limit in terms of LOI to be less than 0.24 wt%, limiting the total plutonium content to no more than 611 ppm, limiting the total plutonium alpha activity to no more than 8,580 microcuries per gram of neptunium, and specifying only a total non-radioactive impurity limit. The original neptunium oxide limits for material inerting, total material mass, total radioactive material mass, and heat generation (watts) from the 9975 SARP were unchanged. The new limits specified in neptunium oxide Letter of Amendment to the 9975 SARP allowed shipments of neptunium oxide to resume between SRS and INL. The first part of the campaign saw fifty (50) cans of neptunium oxide produced by the HB-Line Facility shipped to INL.

CONCLUSIONS

The HB-Line neptunium oxide situation illustrates the need to use bounding content envelopes in Safety Analysis Report for Packaging (SARP) documents. It also shows the value of sampling the final product, which will be offered for shipment, to verify any assumptions or confirm process knowledge. SARPs are legally binding documents that ensure public safety during the transport of radioactive material contained within a designated package. All SARPs must satisfy the regulatory safety requirements of the Code of Federal Regulations (CFR) 10 CFR 71.

For the HB-Line neptunium oxide, the product purity specifications were provided as input to the 9975 SARP content table revision without fully understanding the impacts of such low values. In reality the neptunium oxides content requirements could have been made much broader and still maintain package safety. As a result of the input provided, the limits for neptunium oxide became legally binding and could not be changed without writing a justification for new content requirements and going through another formal regulatory review process.