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Production of Neptunium Oxide from Impure Solutions by Anion Exchange Followed by Oxalate Precipitation

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Abstract: The stabilization of the neptunium solutions stored at the Savannah River Site (SRS) has generated additional recycle solutions that contain a different mix of impurities. A list of expected purities and the known laboratory and production data for purification from those impurities has been accumulated. An evaluation has been performed of the options for modifying the current process to ensure oxide product purity does not significantly change when recycle solutions are processed. This paper discusses the details of the reduction of the major impurities utilizing both known production quality analyses and laboratory flowsheet development data and proposes modifications to the anion wash volumes to remove higher levels of each impurity.

Keywords: Anion exchange, neptunium, plutonium, precipitation, purification, uranium

INTRODUCTION

The Savannah River Site (SRS) has been processing relatively pure neptunium solution through anion exchange and oxalate precipitation to convert the neptunium to an oxide that can be stored and shipped offsite. Product quality requirements are defined by the Safety Analysis Report for Packaging (SARP) (1). Preparations are being made to process relatively

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impure neptunium solutions still stored in shielded canyon facilities. These solutions are scattered between multiple tanks and originated from various purification processes. These solutions have been evaporated to reduce the solution volume and have common characteristics such as high concentrations of impurities (especially iron(III), sulfate and sodium) and relatively low neptunium concentrations ($\sim$1.5 g Np/L). These tanks of solutions have been broadly lumped together and referred to as the impure neptunium solution. Preparations are well underway to purify these solutions by solvent extraction (7.5 volume % TBP in n-paraffin) and then process them into neptunium oxide by the existing anion exchange-oxalate precipitation process. The best estimate has been that purified solutions should be of purity similar to that of the previous relatively pure neptunium solution except that the uranium contamination will be higher. The program goal is to make neptunium oxide from the impure neptunium solution that has purity similar to that prepared from the original pure neptunium. This would allow the utilization of the existing safety basis for storage/shipment as much as possible. Minor modifications of the existing anion exchange process are possible to improve purification as needed.

The current anion exchange production flowsheet was based on historical SRS flowsheets and was customized to the current production campaign. ^{238}Pu was the most significant metallic impurity of concern for shipping/storage of the product oxide because its radioactivity provides the majority of the alpha dose. The amount of alpha dose and the amount of water present in the oxide are the principal factors that determine the rate and quantity of gas generation in product containers. Nitric acid and iron(II) concentration adjustments were made to the anion exchange flowsheet to facilitate ^{238}Pu removal for the current process. The details of the anion exchange flowsheet are shown in Table 1. The overall material flow of the process is shown in Fig. 1.

Table 1. Neptunium anion exchange flowsheet

Load:
8 M HNO_3, 0.05 M Ferrous Sulfamate, 0.02 M Hydrazine
Reductive Wash:
6 Bed volumes 6.4 M HNO_3, 0.05 M Ferrous Sulfamate (0.03 M Fe^{2+} min), 0.05 M Hydrazine
Decontamination Wash:
1-2 Bed volumes of 8 M HNO_3
Elute:
0.17 M HNO_3, 0.05 M Hydrazine
50–60 g Np/L Product solution at 1.5 M HNO_3, Heads and tails cuts discarded with washes

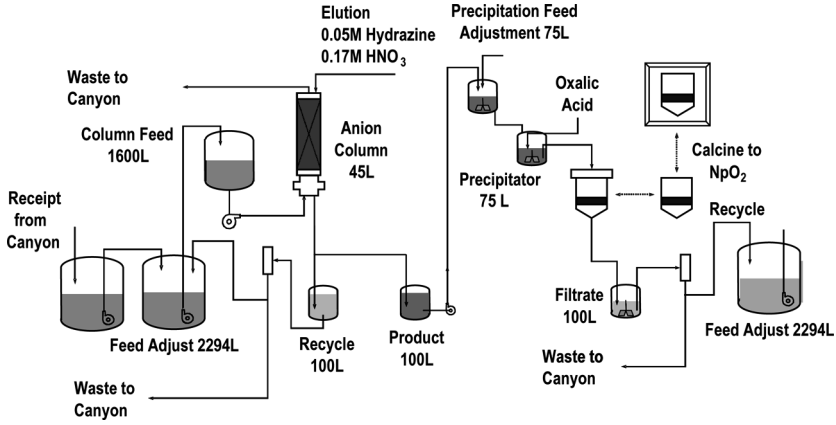

Figure 1. Process flow diagram.

A series of potential impurities for the impure neptunium campaign were identified for consideration. Major impurities such as iron, sodium, manganese, sulfate, and cerium were expected to be removed by the initial purification by solvent extraction. Plutonium and uranium are the primary remaining impurities of interest. The expected purity of the impure neptunium solution after solvent extraction purification is expected to rival that of the original pure neptunium solutions with the exception of uranium. Uranium is expected to be present at $\sim 5\,\text{wt}\%$ on a neptunium basis. Plutonium should be readily removed in the solvent extraction processing but it is still a concern due to its significant impact on the neptunium oxide product and the ample opportunity for re-introduction from hold-up in the process equipment. An evaluation of the existing laboratory and plant production data for both uranium and plutonium was performed to evaluate the need for changes in anion exchange wash procedures to enhance impurity removal.

EXPERIMENTAL

Flowsheet development work in the laboratory was performed in 100 to 200 cc glass columns filled with Reillex^{TM} HPQ strong-base anion resin. Analyses of plutonium were performed by a combination of liquid scintillation, alpha and gamma counting. Analyses for uranium were performed by kinetic phosphorescence analysis.

The production data cited in this paper are the results from samples taken during the processing of multiple kilogram batches of neptunium through a $\sim 40\,\text{L}$ column of Reillex^{TM} HPQ anion resin followed by

the oxalate precipitation of ~1 kg batches of neptunium. Analyses for plutonium were performed by alpha counting and/or mass spectroscopy after separation of the plutonium and neptunium on extractive chromatography resin. Uranium analyses were performed by kinetic phosphorescence analysis. Additional details are contained in reports by Bronikowski (2) and Kyser (3,4).

RESULTS AND DISCUSSION

Plutonium

The original characterization of pure neptunium solution showed the plutonium content on a neptunium basis to be 611 ppm (μg Pu/g Np) or approximately 500 ppm ^{238}Pu. Bronikowski (2) prepared the neptunium oxide for gas generation testing from actual neptunium solution without any wash step to remove ^{238}Pu or other impurities. ^{238}Pu accounts for virtually the entire alpha radioactivity in the neptunium oxide. The decision was made that the existing data on gas generation could be used as the basis for safe shipping and storage of future neptunium material if the ^{238}Pu was less than 500 ppm and the total plutonium was less than 611 ppm.

The production flowsheet that was used for the pure neptunium material utilized a 5–6 bed volume (BV) reductive wash followed by a 1–2 BV decontamination wash. Reductive wash solution contains a reduced nitric acid concentration (6.4 M rather than the 8 M used for the loading step) and 0.05 M ferrous sulfamate to reduce Pu(IV) to the non-absorbing Pu(III) species and wash the plutonium from the neptunium loaded resin bed. Storage time and temperature constraints were placed on the use of the reductive wash solution to ensure a minimal 30 percent removal of the plutonium from the feed solution. Due to conservative decisions in the production facility (i.e. addition of process controls on the reductive wash storage time and temperature), the actual performance of the plant process exceeded the original goal.

The flowsheet development studies (3,4) investigated increasing the reductive wash volumes or reducing the nitric acid concentration of the wash in order to increase the removal of plutonium from the loaded neptunium column. Figure 2 shows results from several reductive wash experiments. In these experiments the fraction of Fe as Fe(II) was steadily increased from 10% of the total Fe to 90% over the 20 BV of each experiment. The nitric acid concentration of the wash solution was varied from 6.0 to 6.8 M. The lower nitric acid concentrations enhanced the removal of the plutonium at the expense of slightly increased neptunium wash losses.

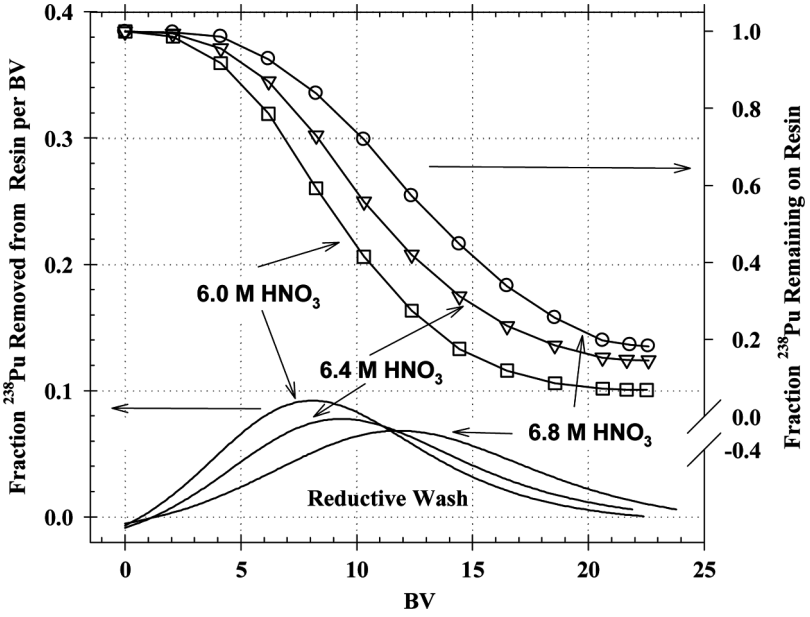

Figure 2. Reductive washing of plutonium in laboratory tests.

Plutonium removal in the anion exchange production process ranged from 30 to 87 percent with an average plutonium removal of 69% over the first 26 cycles of anion exchange (see Fig. 3a). Each cycle of anion exchange consisted of four consecutive column runs, the product from which was collected into two separate product tanks that were analyzed. Only one product tank showed a plutonium removal of less than 43%. The variability of these values was heavily influenced by the variations observed in the first few cycles. If the early results for the initial five cycles are eliminated from the data, the average result for plutonium removal rises to 71% while the relative standard deviation drops from 18% to 11%. The amount of plutonium impurity dropped from 510 ppm in the feed solution to 150 ppm in the anion product solution. A summary of these data are included as Table 2. These data were provided by the facility engineering organization and are based on process analyses that have some error that is due to the unexpected presence of ^{239}Pu that was not accounted for in the assumed isotopic distribution. For this discussion it is assumed that these analyses can be directly compared to each other to determine impurity removal.

The neptunium oxide product was also analyzed for plutonium impurity. Figure 5a shows the preliminary production analyses for

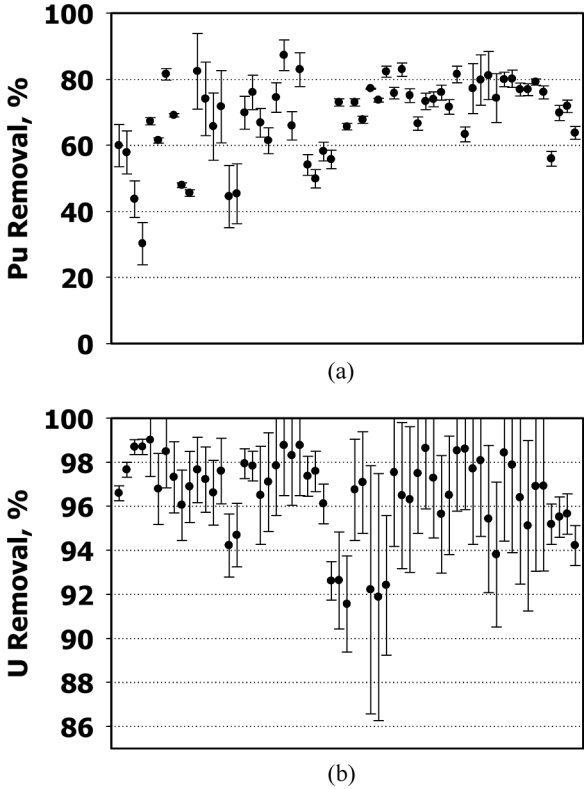

Figure 3a, b. Plutonium and uranium removal in the production process over 59 runs.

plutonium on the oxide produced from the initial 37 cycles of anion exchange (147 individual product samples from several hundred precipitation batches). Unfortunately much of this data was calculated using the feed solution isotopic composition for plutonium rather than an experimentally determined value. Later in the campaign it was recognized that the plutonium isotopic distribution was affected by ^{239}Pu contamination in some initial batches. ^{239}Pu contamination diluted the major isotope of interest ^{238}Pu and decreased the accuracy of the results. The results reported in Fig. 5a for plutonium are based on an assumed isotopic composition of $\sim$82% ^{238}Pu.

If additional plutonium removal were required for processing of the impure neptunium solutions, additional reductive wash volume could be used. Alternatively, the reductive wash acid concentration could be dropped from 6.4 M HNO_3 to 5 M HNO_3 with increased neptunium

Table 2 . Production anion process results

Anion product	Pu, ppm		U, ppm	
Ave	155	33%	127	55%
Min	66		35	
Max	338		330	
Ave	149	17%	135	22%
Min	69		48	
Max	244		330	
Feed solution				
Ave	509	16%	3681	11%
Min	373		2623	
Max	610		4449	
Ave	527	12%	3680	10%
Min	373		2623	
Max	610		4449	
Anion process	**Pu removed**		**U removed**	
Ave	68.5%	17.6%	96.5%	2.0%
Min	30.2%		91.6%	
Max	87.2%		99.0%	
Ave	71.0%	11.4%	96.3%	2.0%
Min	44.5%		91.6%	
Max	87.2%		98.8%	

losses of 11%. For details refer to the flowsheet references by Kyser (3,4). The expected DF for plutonium in the second pass of solvent extraction (reducing flowsheet) is expected to be very high (5) (10^4) and additional washing for plutonium removal should not be required. However, the amount of contamination of the solvent extraction product with plutonium from tank heels and piping transfers is a concern. Additional flushing was planned to reduce this risk.

Uranium

The pure neptunium solution contained $\sim$0.5 weight percent uranium on a neptunium basis as an impurity. The neptunium oxide for gas generation testing was prepared from plant neptunium solution without any wash step that would have removed uranium. The uranium content of the anion exchange product was characterized by Bronikowski (2) but the uranium content in the final neptunium oxide produced by oxalate precipitation was not measured.

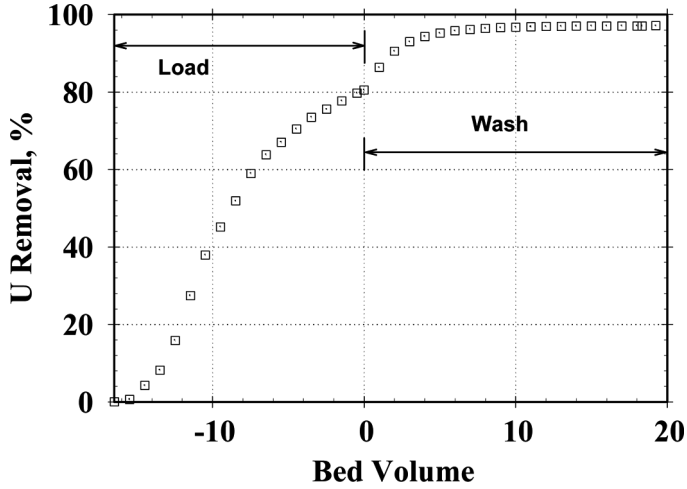

Figure 4. Uranium removal in laboratory tests.

Rudisill (6) investigated the decontamination of a large amount of uranium from a plutonium solution by anion exchange and showed that significant uranium was rejected during the load step (83% or a DF = 5.8). Figure 4 shows the uranium removal profile data from that study. A single additional BV of 8 M HNO_3 wash raised the uranium removal to 88.8% (DF = 8.9). A rinse with a total of 7 BV of 8 M HNO_3 wash raised the uranium removal to 98.9% (DF = 94). The lower HNO_3 concentration used in the neptunium production process (6.4 M HNO_3) should be more effective at uranium removal than the 8 M HNO_3 studied by Rudisill due to the reduction in the uranium distribution coefficient. Although the amount of uranium in the neptunium oxide that was used for gas generation was not measured, a value has been estimated. Based on the original value (4670 ppm uranium) and the removal observed by Rudisill during loading with one BV of heads cut during elution (88.8% or DF = 8.9) and an assumed DF of 10 via oxalate precipitation (from plant observed data described later in this section), a value of 52 ppm uranium has been calculated as a realistic estimate for the test material in the neptunium oxide gas generation experiments.

Production analyses of anion exchange product samples during the first 26 cycles of anion exchange showed 127 ppm uranium (or 96.5% removal). Based on Rudisill's work, the uranium in the current production anion exchange product solutions would be expected to be < 50 ppm (or 98.6% removal). The uranium removal observed in the plant neptunium process is lower than that observed in the

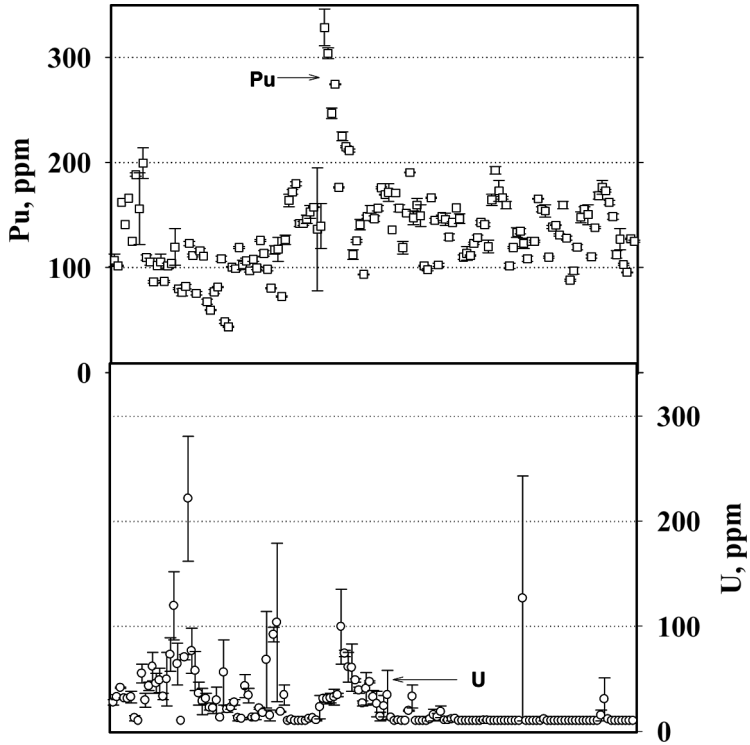

Figure 5a, b. Plutonium and uranium impurity in final neptunium oxide product.

plutonium–uranium work. The removal of uranium in the initial 26 anion exchange production runs is shown in Fig. 3b.

Unlike plutonium, uranium is known to have significant solubility in oxalate precipitation. Production analyses of neptunium oxide product from the first 37 cycles of anion exchange show an average uranium impurity level of 26 ppm. Most of the high uranium values are in the early product and if only cycles 20–37 are included the average drops to 13 ppm uranium (which reflects a DF = 10 for oxalate precipitation). The oxide product analyses for the material from the first 37 cycles of anion exchange are shown as Fig. 5b. These data reflect an average uranium removal of 96.3% (DF = 29) for the anion process and a total uranium removal of 99.3% (DF = 139) for anion exchange and precipitation combined.

The solvent extraction processing of the impure neptunium was not expected to remove any uranium (5) and based on recent analyses, the total uranium impurity in all the impure neptunium solutions together

averaged ~5.5 wt % (or 55000 ppm). Applying the DF estimated from the Rudisill experiments (DF = 94 for 7 BV of 8 M HNO_3) would result in anion exchange product solution with 585 ppm uranium (1896 ppm using the observed DF from the current anion process). Using the process observed DF for anion exchange and oxalate precipitation (DF = 139) would result in a neptunium oxide product of 396 ppm uranium compared with the 52 ppm value that was estimated for the oxide tested for gas generation testing. Since these projections indicate a significant increase in the uranium content of future oxide prepared from the impure neptunium solutions, process changes were evaluated to increase the uranium removal in the anion exchange process.

Increasing the volume of either the reductive wash or decontamination wash solutions will increase the removal of uranium by the anion exchange process. An increase in the uranium DF by a factor of ten should be obtained by washing with an additional 6 BV of decontamination wash. The uranium removal from increased washing was estimated by evaluation of Rudisill's raw data. There is considerable uncertainty in this evaluation so the success of this process change will have to be evaluated by measurements on the initial runs. Increases in the reductive wash volume would be similarly effective but increases in the reductive wash solution would generate additional waste from the ferrous sulfamate reductant and unless increased levels of plutonium were also found to be a problem, the decontamination wash increase would be a better option. A lowering of the wash acid concentration would also be expected to increase the removal of uranium but precise data allowing the prediction of the effect is not readily available. Therefore, that approach has greater uncertainty for adequate uranium removal. Lowering of the wash acid concentration would also increase the neptunium losses to the wash.

A separate concern with additional uranium was its effect on the loss-on-ignition (LOI) measurements used to indicate the level of water present in the product oxide. This effect is expected to be due to the weight loss of UO_3 to U_3O_8 or UO_2 as the neptunium oxide is heated above the production calcination temperature of 650°C during LOI measurements. A LOI test to 950°C is expected to convert significant UO_3 to U_3O_8. Although the test conditions are not expected to allow reduction to UO_2, the calculation to determine the amount of uranium necessary to affect the LOI measurements significantly was calculated on the reduction of UO_3 to UO_2 as a limiting case. Conversion of UO_3 to UO_2 results in a 5.6% weight loss for pure UO_3 or an additional 0.0056 wt% loss for a sample of NpO_2 with 1000 ppm present. With a shipping limit of 0.24 wt% for LOI, anything up to 1000 ppm UO_3 impurity should not significantly affect the LOI test result.

General Comments

The production results included were analyzed in duplicate. Those duplicate analyses were used to estimate the precision of the results as one-half the difference between the duplicate values. The error bars shown in Figs. 3 and 5 reflect this estimate of precision. The plutonium and uranium removal data generally agreed to within ± 6 percent. The stated uncertainty for the analytical methods was 10 percent for plutonium and 17 to 21 percent for uranium.

The results from roughly the first half of this production campaign were available at the time that this analysis was performed. Sufficient data were accumulated during this time to provide a reasonable picture of the ability of the process to produce a consistently pure oxide product. Future processing is expected to resume at a similar level of quality and consistency.

CONCLUSIONS

A combination of laboratory flowsheet data and neptunium production data have been used to evaluate impurity concentration changes as production shifts from the processing of relatively pure neptunium feedstock to impure recycled solutions containing dilute neptunium. In an attempt to limit the uranium in the neptunium oxide product to the levels that were tested for the original shipping evaluation, an increase in the anion exchange washing has been recommended. By increasing the decontamination wash by 6 BV over the amount used in the recent campaign, it is anticipated that the 10-fold increase in uranium impurity in the feed solution from the process can be removed. Success of this process change will be monitored by analysis in the initial batches and further modification in the wash volumes will be considered, if appropriate. Other impurities are not expected to pose a significant challenge. Plutonium would be the impurity that would cause the most impact but this impurity appears to have been controlled by the solvent extraction flowsheet used and additional equipment flushes.

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