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PROCESS DEVELOPMENT FOR PLUTONIUM-238 PRODUCTION AT OAK RIDGE NATIONAL LABORATORY

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The third chemical processing campaign conducted at Oak Ridge National Laboratory (ORNL) with irradiated neptunium oxide–aluminum cermet targets produced plutonium-238 oxide product meeting purity specifications for space power applications. This is a major step for the Plutonium-238 Supply Program toward reestablishing production. This summary highlights results to date and presents focus areas of current activities to improve process efficiency and to increase production rate.

I. INTRODUCTION

ORNL has restarted domestic production of ^{238}Pu for use in space power applications. This mission involves producing neptunium targets for irradiation in Department of Energy research reactors, processing the irradiated targets to separate and purify the produced plutonium, and transferring the heat-source plutonium oxide (HS-PuO_2) product to Los Alamos National Laboratory (LANL). Under current plans for constant-rate production of ^{238}Pu heat sources,[1] ORNL will initially achieve production at an average rate of ~400 g/y by the end of fiscal year (FY) 2019. Scale up to 1.5 kg/y will occur by increasing the number of processing campaigns per year over the 2020–2025 time frame.

Chemical processing plays a key role for the success of the effort. In a performance audit report published before Campaign 3 in September 2017, the Government Accountability Office identified challenges with chemical processing that could affect the ability of the Department of Energy to meet NASA's demand for ^{238}Pu and radioisotope power systems.[2] The report noted the product material from initial demonstrations did not meet space flight specifications because they contained impurities. The report also highlighted the need for additional staff and equipment resources to scale up processing to achieve production goals. As discussed below, the first challenge has been addressed, and plutonium-238 oxide meeting General Purpose Heat Source (GPHS) impurity specifications was produced in the most recent processing campaign. Activities are in progress to overcome the second challenge.

II. APPROACH

A simplified process diagram for chemical processing in ^{238}Pu production is shown in Fig. 1. These steps are conducted using existing equipment at the Radiochemical Engineering Development Center (REDC) in heavily shielded hot cells and glovebox laboratories suitable for manipulation of alpha-emitting isotopes and highly radioactive fission products. Although REDC has five decades of demonstrated capability in production of ^{252}Cf and other actinides,[3] the Plutonium-238 Supply Program will utilize the facility and equipment using a new process flowsheet and at a larger scale of production.

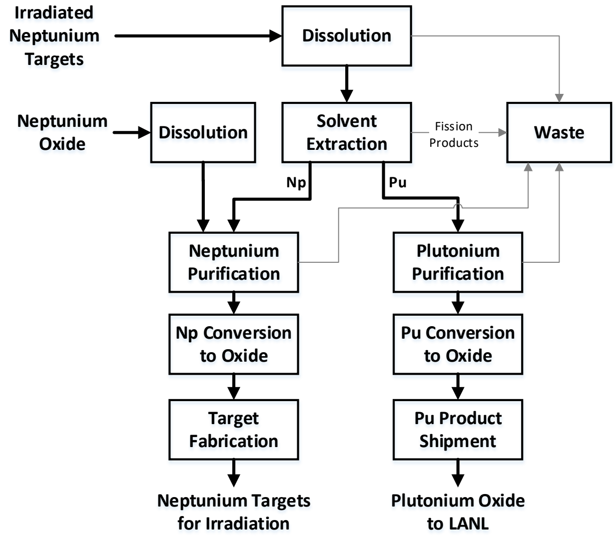

Fig. 1. Simplified process diagram.

Chemical processing is needed to prepare the NpO_2 feedstock for target fabrication. This step involves dissolution of the oxide material and treatment to remove decay products and other impurities from the Np. Removal of the ^{233}Pa daughter of ^{237}Np significantly reduces the radiation dose to workers during subsequent steps conducted in containment gloveboxes to convert the neptunium to oxide powder, to form cermet pellets from neptunium oxide and aluminum powders, and to fabricate targets containing the pellets.

After irradiation, neptunium targets are dissolved in a two-step process; the aluminum in the cladding and

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cermet pellets is dissolved in caustic nitrate solution and discarded as waste, then the remaining actinide and fission product oxides are dissolved in nitric acid. Solvent extraction is employed as the primary method to separate the plutonium and neptunium from fission products and to separate the plutonium from the bulk of the neptunium. The plutonium-containing stream from solvent extraction is further purified by ion exchange processing and then converted to oxide. The neptunium is further purified by ion exchange processes and converted to NpO_2 for the fabrication of new targets.

III. PROGRESS TOWARD OPTIMIZING THE CHEMICAL PROCESS

Previous processing demonstrations (Campaigns 1 and 2) showed promise for the approach depicted in Fig. 1; however, the plutonium oxide products of those campaigns contained undesirable levels of impurities, notably phosphorus and thorium.[4] The thorium is present as an impurity in the source neptunium oxide material, whereas the phosphorus appears to be introduced into the plutonium product stream from solvent extraction by degradation of the tributyl phosphate extractant.

The focus of Campaign 3 was to generate HS-PuO_2 meeting GPHS impurity specifications.[5] The campaign was conducted using a prototypic campaign batch size of 63 NpO_2-aluminum cermet targets, 49 of which had been irradiated for 3 cycles in the High Flux Isotope Reactor, and 14 irradiated for 2 reactor cycles. The processing steps used in Campaign 3 and their primary functions are shown in Fig. 2. Key differences from previous campaigns include changing the solvent extraction step from a single cycle to two cycles and the addition of an anion exchange step for purification of the plutonium in the stream generated by the first solvent extraction cycle.

Solvent extraction in two cycles eliminates use of sodium nitrite as a reductant for separation of Pu from Np, which removes the need to separate sodium from the separated Np and reduces waste generation. For the first cycle of solvent extraction, the feed is adjusted to maximize Pu and Np in the Pu(IV) and Np(V) oxidation states. The plutonium is selectively extracted, and the raffinate containing neptunium and fission products becomes the feed for the second solvent extraction cycle.

The Pu stream from the first solvent extraction cycle was conditioned for anion exchange processing by acidification and adjustment of oxidation state to Pu(IV) using hydrogen peroxide.[6] The anion exchange runs were conducted similarly to traditional processes for loading, washing, and elution of plutonium.[7] Fractionation of the eluent permitted the collection of a Pu solution with the Th and the majority of the Np removed, without the use of a reductive strip. The Pu product from anion exchange was measured to be free of P and suitably low in Th, Np, and other critical impurities to enable final purification by cation exchange loading and conversion to oxide by calcination to PuO_2, a REDC process used to produce curium oxide.[8]

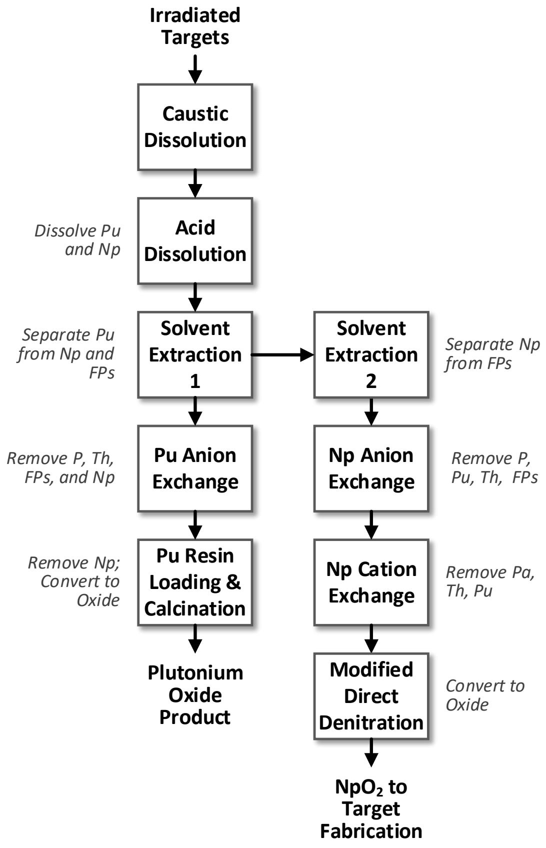

Fig. 2. Process steps used in Campaign 3, listing primary functions of each step.

Campaign 3 generated 250 g of HS-PuO_2 product, which was found to be of excellent quality. The ^{238}Pu content of 85.1% of total Pu isotopes and ^{236}Pu content of 2 ppm met the GPHS specification.[9] Table I presents results of ORNL analyses of impurities in samples of product from two calcination batches; the levels of all impurities were measured to be well below the GPHS specification limits. Analyses by LANL were in good agreement with the ORNL measurements and verified phosphorus at nondetectable levels below GPHS specification.

The neptunium stream from the first cycle of solvent extraction was further purified for recycle by a combination of solvent extraction and ion exchange steps. The feed solution for the second cycle of solvent extraction was adjusted to maximize Np as Np(VI) to separate the Np away from the majority of aqueous soluble fission products. Analogous to the Pu anion exchange processing, a Np product solution was collected having the majority of Pu and Th removed. Further purification by cation exchange was used to remove Pa, as well as Pu, Th, and other cationic contaminants, from each batch of Np solution before conversion to oxide by modified direct denitration.[10]

TABLE I. Impurity analysis of HS-PuO_2 from Campaign 3 compared with GPHS specifications

	Batch 1	Batch 2	GPHS spec.
	Actinide impurities, wt%		
^{232}Th	0.07	0.12	≤0.5
^{234}U	0.04	0.06	≤0.5
^{237}Np	0.03	0.30	≤0.5
Total actinides[a]	0.17	0.48	≤1.0
	Non-actinide impurities, ppm[b]		
Al	<50	<11	≤500
B	<5	<200	≤20
Be	<0.05	<0.1	≤5
Ca	<50	<100	≤500
Cd	<0.05	<0.05	≤50
Cr	12	12	≤500
Cu	<0.1	<10	≤200
Fe	<25	<35	≤1000
Mg	<50	<11	≤100
Mn	<0.5	<1	≤50
Mo	<0.5	<0.5	≤250
Na	<50	<75	≤250
Ni	<0.05	<5	≤500
P	<40[c]	<148[c]	≤25
Pb	<2.5	<5	≤100
Sn	30	<50	≤50
Zn	<0.5	<10	≤50

[a] Atomic masses that were below detection at 0.05 wt% included 228, 229, 230, 233, 235, 236, 243, 244, 245, 246, 247, and 248.
[b] < measurements are below detection limits at those values
[c] ORNL measurements; P measured by LANL at <10 ppm.

IV. ACTIVITIES TOWARD INCREASING SCALE OF PRODUCTION

Campaign 3 produced acceptable HS-PuO_2 meeting ^{238}Pu content and impurity specifications; however, the rate was insufficient for full-scale production. Due to the limited scale and developmental nature of several process steps, the campaign required a large number (~40) of operations over a protracted schedule (~230 days). To meet the projected production rate over the next several years, the duration of a campaign must be improved to approximately 90 days for Campaigns 5–7 in FY 2020, 70 days for Campaigns 9–14 in FY 2022, and approximately 55 days for full-scale production at 1.5 kg/y.

Process improvements are in progress to reduce the duration of future campaigns. Larger ion exchange columns will be installed to increase batch size of Pu anion exchange and Pu cation exchange by up to 3 times and Np anion exchange by a factor of 2. Campaign 4, to be conducted in the second half of FY 2019, will demonstrate the scaled-up process steps and is projected to comprise 20 process operations over 110 days.

Additional improvements may further increase process efficiency. Cation exchange processing has been developed to remove Th, Pu, and Pa from dissolved neptunium oxide and recycled Np. This will result in low levels of Th in irradiated targets for processing in Campaign 5 forward, which may enable further process simplification. In addition, diluent washing for removing P from recycled Np solution will be tested in Campaign 4 to evaluate the possibility of eliminating the need for the Np anion exchange step, to improve production rate and to reduce chemical usage. The potential efficiency improvements from additional equipment modifications will continue to be evaluated with data from upcoming campaigns.

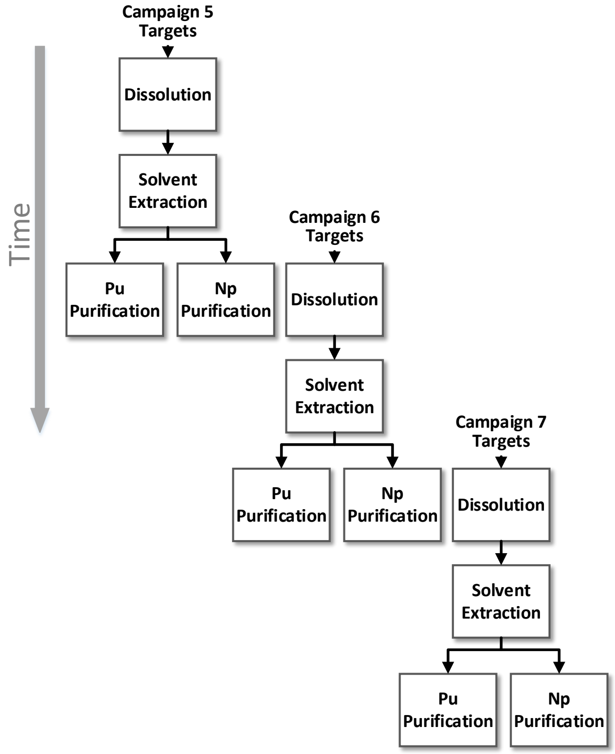

Fig. 3. Depiction of overlapping campaigns.

Improvement of the production rate is also to be achieved through increased staffing and efficiency of workflow.[11] Contrary to earlier campaigns conducted sequentially, Campaigns 5 and beyond will include parallel processing operations and potentially overlapping campaigns (see Fig. 3). To move to the desired level of operation, workforce development is paramount to ensure that enough trained staff are available to conduct multiple simultaneous processing operations, to maintain efficient materials management, and to balance facility operations.

V. SUMMARY AND OUTLOOK

Chemical processing is a central part of the effort to reestablish domestic production of HS-PuO_2 for deep-space missions. Perfecting chemical processing, both in terms of generating product meeting specifications and establishing an enterprise capable of achieving production goals, is required for success of the overall NASA/DOE constant-rate production plan. The most recent campaign generated plutonium oxide product meeting impurity specifications in a prototypic batch size. Efforts over the next several campaigns are focused on improving efficiency, increasing rate, and establishing processes and a workforce for sustained, full-scale production.

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