PROCESS CHEMISTRY FOR THE PRODUCTION OF PLUTONIUM-238

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Abstract—*The natural decay heat (0.57 W/g) from the radioisotope ^{238}Pu provides the thermal energy source used by radioisotope power systems to generate electricity for operation of instrumentation, as well as heat to keep key subsystems warm for deep space missions. Plutonium-238 is produced by irradiation of neptunium-237 in a nuclear reactor with a relatively high thermal neutron flux. NASA and the Department of Energy have reestablished a ^{238}Pu supply capability using existing facilities and reactors. Target rods containing NpO_2 are currently fabricated at Oak Ridge National Laboratory (ORNL) and irradiated in the ORNL High Flux Isotope Reactor, but soon rods will be irradiated in the Advanced Test Reactor at Idaho National Laboratory. Irradiated targets are processed using chemical separations at the ORNL Radiochemical Engineering Development Center to recover the plutonium product and unconverted neptunium for recycle. The recovery of neptunium and plutonium depends heavily on modification of a traditional tri*-n-*butyl phosphate–based full cycle chemistry. The $^{238}PuO_2$ product is shipped to Los Alamos National Laboratory for fabrication of heat source pellets. Key activities, such as the transport of the neptunium to ORNL, irradiation of neptunium, and chemical processing to recover the newly generated ^{238}Pu, have been demonstrated with an initial amount of 350 g PuO_2 produced. This paper examines chemical processing necessary to the approach to producing new ^{238}Pu.*

1. INTRODUCTION

The Department of Energy (DOE) is responsible for maintaining the national capability to support the design, development, production, deployment and safety of radioisotope power systems for NASA and national security missions. DOE and its predecessor agencies have been producing radioisotope power systems for more than 50 years. Radioisotope power systems uniquely enable missions that require a long-term, unattended source of electrical power and/or heat in harsh and remote environments. These systems are reliable, maintenance-free, and capable of producing heat and electricity for decades. Plutonium-238 serves as the heat source for all radioisotope power systems launched by the United States.

Radioisotope power systems have proven highly successful in the United States and have been used on 27 space missions to date. NASA, in partnership with DOE, has deployed radioisotope power systems on missions to the Moon, Mars, and the outer planets. Four active radioisotope power systems–powered missions continue to provide information at Mars, Saturn, Pluto, and beyond the boundary of our solar system.

The ^{238}Pu production process consists of the fabrication of ^{237}Np targets, irradiation of the targets in a nuclear reactor, and recovery of ^{238}Pu from the irradiated targets through chemical extraction. In the past, ^{238}Pu was produced at DOE's Savannah River Site in South Carolina on an incremental basis during large-scale production of weapons-grade plutonium, using reactors that have been shut down. The last ^{238}Pu production in these reactors occurred in 1988. After DOE stopped producing ^{238}Pu, DOE's remaining inventory, supplemented by purchases from Russia, has been used to continue to supply power systems. NASA and DOE have begun a multiyear project to reestablish the capability to make ^{238}Pu using existing DOE facilities. This paper describes that project and the status of the effort.

2. BACKGROUND

To enable reasonable production rates, production of ^{238}Pu requires irradiation of ^{237}Np in a nuclear reactor with a high neutron flux. DOE has selected two research reactors with sufficient flux for this purpose—the Advanced Test Reactor at Idaho National Laboratory (INL) and the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL).

Figure 1 outlines the production of ^{238}Pu, which involves the following five steps:

1. Neptunium oxide in storage at INL must be put into shipping containers and shipped to ORNL for ^{238}Pu production.

2. Neptunium oxide that has been in storage requires purification to remove its decay daughter, ^{233}Pa, which

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emits a low-energy gamma ray that contributes to worker dose during subsequent target fabrication activities. Purification and recycling of neptunium require conversion to an oxide form for target fabrication.

3. Targets are fabricated by blending NpO_2 with aluminum powder and pressing the mixture into a pellet. Multiple pellets are then clad in an aluminum tube and sealed by welding.

4. Targets are irradiated in either the Advanced Test Reactor or HFIR. Irradiation times vary from one to six cycles, depending on the specific location in the reactor core and the buildup of undesirable isotopes such as ^{236}Pu.

5. Irradiated targets go through a series of chemical processing steps to recover and purify both neptunium and plutonium. Plutonium is shipped to Los Alamos National Laboratory (LANL), and neptunium is recycled back to target fabrication.

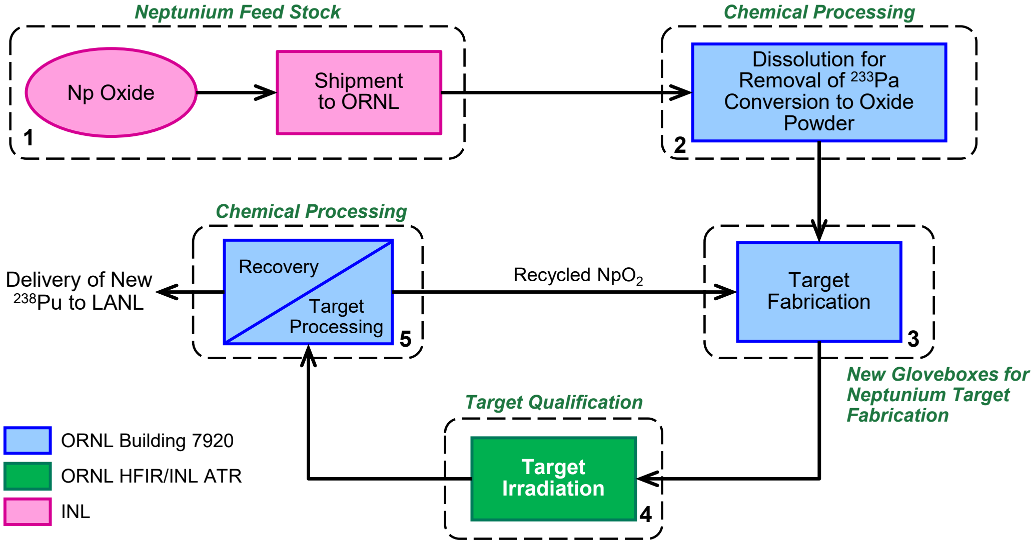

Figure 1. Plutonium-238 production flow diagram.

Although ^{238}Pu was previously produced at the Savannah River Site, the processes must be modified to use existing DOE infrastructure. There are two major areas requiring development.

First, a new small, dense target for irradiation of NpO_2 must be developed. The Savannah River Site targets were very large and not very dense (only 6 vol% NpO_2 in the aluminum matrix). Current DOE research reactors have a much smaller volume and must be loaded to a density of approximately 20 vol% NpO_2. The problem is that a small portion of the ^{237}Np fissions, releasing significant amounts of fission heat; consequently, targets must be designed to operate at temperatures lower than the melting point of aluminum (~650°C).

Research staff at both Savannah River National Laboratory[1,2] and INL[3] have identified process improvements to reduce costs and wastes using solvent extraction to recover Np/Pu instead of the anion exchange process used originally at the Savannah River Site. This process modification also requires additional development and testing.

The process chemistry is affected by the ^{238}Pu concentration as well as the presence of fission products. The high radiation fields from the fission products cause the processing chemicals to degrade. The efficiency of separation and recovery is significantly impacted by these changes in process chemistry. This paper will describe the current status of development underway to test and scale up the various process steps required to produce ^{238}Pu.

3. STATUS OF DEVELOPMENT

This project plans to develop a robust set of processes modified to account for this particular combination of Pu/Np so that an average annual production level of 1.5 kg/y of bulk plutonium oxide can be sustained for many years. A testing program was developed so that the various parts of the overall project could be demonstrated at small (milligram to gram) levels and scaled up to the kilogram per year level. Currently, the testing program is scheduled to be complete and transition into pilot operations at the end of 2019. Final scale up to 1.5 kg/y is anticipated to be complete by 2026. The following sections describe development efforts to date.

Neptunium transfer—Most of the nation's supply of separated ^{237}Np resides in storage vaults at INL. Neptunium target feed material will be shipped to ORNL from INL on a just-in-time basis in Department of Transportation (DOT) 9975 shipping containers. The DOT 9975 container represents a robust package for confinement of the $^{237}NpO_2$.

The DOT Certificate of Compliance for this container has been updated to include the $^{237}NpO_2$ payload. The containers are approved for up to 6 kg of $^{237}NpO_2$.

Target fabrication—The production target consists of a stack of cylindrical pellets containing the aluminum $^{237}NpO_2$ material sealed within an aluminum tube (clad). An exploded view is shown in Figure 2. The $^{237}NpO_2$ is blended with aluminum powder and formed into pellets by pressing the material in a die at high pressures.

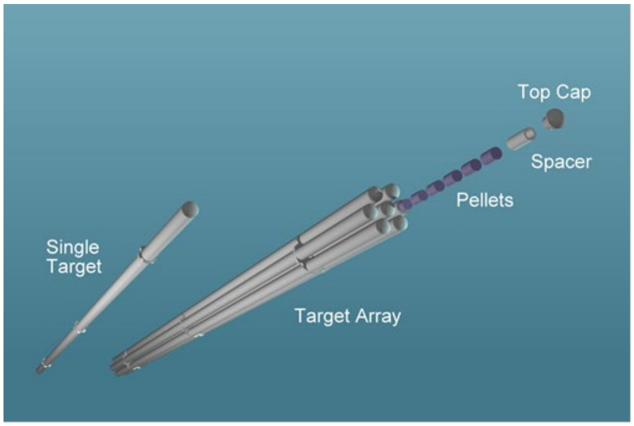

Figure 2. Illustration of NpO_2/Al cermet target used to produce ^{238}Pu.

Pressing the oxide target material with the substrate aluminum base material forms a ceramic/metallic compound typically referred to as a *cermet*. Currently, enough NpO_2 and aluminum powder for single pellets are separately weighed and metered into individual vials using automated dosing equipment. The vials are then mixed, dispensed into a die, and pressed to make a pellet. Pellet quality control requires fabricating pellets to carefully controlled weights and dimensions. All weights and dimensions are measured on a one-pellet-at-a-time basis. The cermet pellets that pass the quality control requirements are loaded into aluminum tubes, and the ends of the tubes are welded to form a single target assembly. Individual targets are placed into target holders to form target arrays, with the number of targets per array assembly dependent upon the irradiation space. Currently irradiations in HFIR are based on bundles of seven targets. Eventually, positions at the Advanced Test Reactor will be used for additional capacity.

Target design, testing, and qualification—Figure 3 shows the irradiation pathway to produce ^{238}Pu. Neptunium-237 oxide is used as the feedstock. The optimal neutron flux is a thermal neutron flux on the order of 10^{14} n/s/cm^2. High energy neutrons and photons (greater than 6 MeV) result in production of ^{236}Pu (shown on the left side of Figure 3), which is undesirable. Thermal neutron irradiation of ^{237}Np results in a neutron capture followed by a beta decay that makes ^{238}Pu. There are additional neutron captures indicated on the right side of the figure that make ^{239}Pu and ^{240}Pu as shown in the upper right corner of Figure 3. The targets and irradiation conditions are designed to maximize ^{238}Pu and minimize other isotopes. The goal of the irradiation scheme is to produce Pu that consists of >85% ^{238}Pu. Most of the balance is ^{239}Pu and ^{240}Pu, and ^{236}Pu is measured in parts per million.

The bottom right side of Figure 3 depicts fission of ^{237}Np and ^{238}Np occurring during irradiation. This fission generates heat which must be removed to keep targets below the melting point of aluminum (650°C).

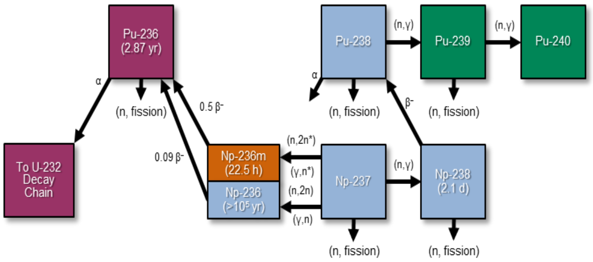

Figure 3. Neutron irradiation and isotope decay in HFIR from feedstock (^{237}Np) to production (^{238}Pu).

Chemical processing—The chemical process steps are shown in Figure 4. Steps are coded with numbers that indicate the status of the development of those steps below.

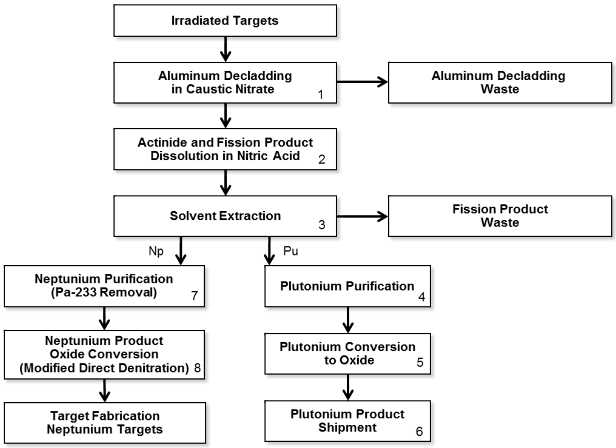

Figure 4. Proposed processing flow sheet for ^{238}Pu of over 160 targets neptunium recovery.

(1) *Aluminum dissolution*—Aluminum dissolution is exothermic and requires careful process controls to avoid overheating the reaction mixture. Sodium hydroxide is metered into a tank containing the target rods and sodium nitrate this technique has been used for four dissolutions to date.

(2) *Actinide and fission product dissolution in nitric acid*—After aluminum has been dissolved in caustic and this solution removed, the actinide (Np+Pu) oxides, as well as many of the fission products, are dissolved in a solution of concentrated nitric acid. The dissolution takes place at ~100–110°C over many hours. After dissolution, the chemical valences of both plutonium and

neptunium are adjusted before solvent extraction. Actinide dissolution will need to be tested several more times at a prototypic level.

(3) *Plutonium/neptunium separation using solvent extraction*—Effective separation of the plutonium/neptunium/fission product (FP) mixtures requires control of the valence states of both plutonium (which can exist as Pu^{+3}, Pu^{+4}, and Pu^{+6}) and neptunium (which can exist as Np^{+4}, Np^{+5}, and Np^{+6}). Techniques for valence control have been developed over several years.

The equipment used for each Pu recovery campaign has seen changes to enable more effective valence adjustment and control. The current valence control method under consideration will be tested to minimize the use of reductant in the separations conducted in a three-bank set of small-volume mixer-settlers. The separations flowsheet, depicted in Figure 5, begins with adjusting the valences as closely as practical to Np^{+5} and Pu^{+4}. The Np/Pu/FP mixture enters the middle of the top bank of mixer-settlers, or A-bank. The Pu^{+4} is extracted into the organic phase, which flows from right to left and into the middle of the B-bank. The fission products and Np^{+5} flow to the right and exit. In the B-bank, a reductant is added to reduce Pu^{+4} to Pu^{+3}. The Pu^{+3} is stripped from the organic phase back into the aqueous phase and exits as the plutonium product. The aqueous stream containing plutonium is the routed to the third (C) bank where a diluent wash is conducted to remove phosphorous. The plutonium product is then sent on to anion exchange for additional purification.

The neptunium in the aqueous stream exiting the A-bank is separated from fission products using a second solvent extraction process as shown in Figure 6. The neptunium feed is adjusted to make Np^{+6}., which is extracted in the A-bank and the loaded organic is fed to the B-bank. In the B-bank, the Np^{+6} is reduced to Np^{+5} and removed from the organic phase. The C-Bank provides additional diluent wash stages to remove phosphorus.

Methods of valence control have been developed to hold valences in specific states while monitoring valences to see if disproportionation occurs. Initially the use of ultraviolet-visible spectroscopy was employed to monitor valence states and examine the kinetics of disproportion in glovebox tests. Similar equipment will be used in the hot cell facility to support scale up to production-level operations. Data from the tests will be used to establish scale-up requirements. In tests conducted to date, valence control has been moderately successful. The Np product is relatively free from Pu. However, the Pu product contains significant amounts of Np and requires further purification. Further tests will be needed.

(4) *Plutonium purification*—ORNL is currently working closely with LANL to ensure that the product purity of the newly generated PuO_2 is adequate for use in the LANL process that produces the encapsulated PuO_2 pellets. Testing indicates that the plutonium product from the solvent extraction step will have too much Np for use as final product. Current efforts focus on adjusting the valences so that valences are Pu^{+4} and Np^{+6}. The solution is adjusted to high acidity and passed through a column containing anion exchange resin, and Pu/Np will load on the resin as the nitrate complex. After loading, the column is washed with nitric acid. The Th and Np are eluted first and collected separately. The remaining plutonium is then stripped off the resin at low acidity.

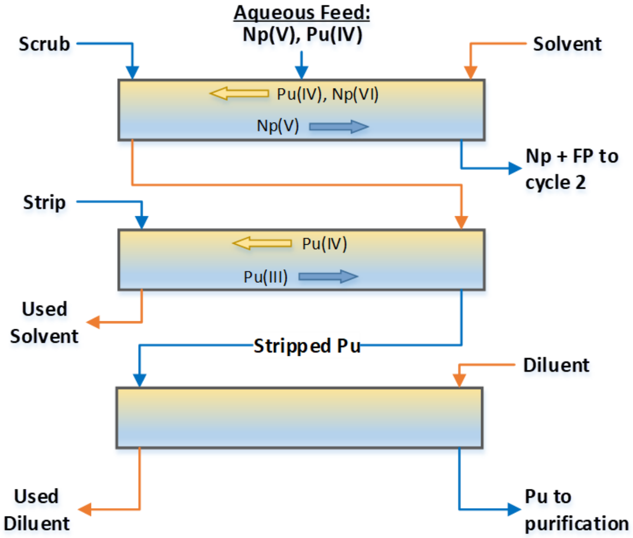

Figure 5. Current flowsheet for Pu extraction and partitioning. Organic streams are shown in yellow, and aqueous streams are shown in blue. Plutonium is extracted in the A-bank, and the B-bank is designed to reduce Pu(IV) to Pu(III). The C-bank is used for diluent washing of the Pu in order to remove P.

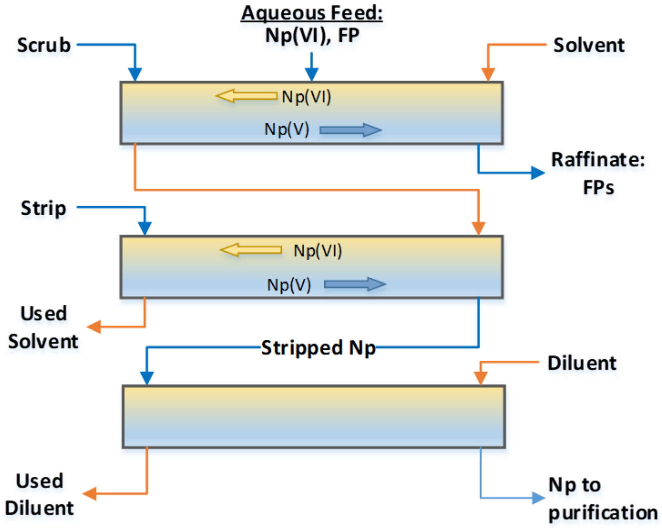

Figure 6. Current flowsheet for Np extraction and stripping. Organic streams are shown in yellow and aqueous streams are shown in blue. Neptunium is extracted in the A-bank and the B-bank is designed to reduce Np(VI) to Np(V). The C-bank is used for diluent washing of the Np in order to remove P.

(5) *Plutonium conversion to oxide*—The purified plutonium is then loaded onto a column containing cation resin, placed in a furnace, and heated to >500°C to destroy the resin and produce an oxide product. The process of loading plutonium on the resin provides additional decontamination from Np. This technique is based on existing methods of loading curium onto a cation exchange resin. The resin is then fired to convert the actinides to an oxide.

(6) *Plutonium product shipment*—Plutonium oxide will be placed in small screw-top containers and transferred out of the cell bank. These containers will then be placed into a can that is compatible with the storage requirements at LANL. The can will be welded shut and transferred into a shipping package that is then shipped to LANL. Currently, ORNL is designing and procuring a set of glove boxes to move the Pu product into an appropriate shipping configuration. The capability to make

shipments to LANL is expected to be operational by the first quarter of calendar year 2020.

(7) *Neptunium purification*—Currently, anion exchange is used to remove the remaining fission products from the neptunium used in target fabrication. Since neptunium decays to ^{233}Pa, which has a 27-day half-life and emits approximately 300 keV gammas as it decays, it must be removed to minimize personnel dose before target fabrication. If not removed from the ^{237}Np, its activity would result in significant doses to the target fabrication staff. Protactinium-233 is removed by passing the aqueous neptunium nitrate solution through a DOWEX cation exchange column resulting in a relatively low-dose neptunium nitrate solution, which is transferred out of the cell on a just-in-time basis.

(8) *Neptunium product oxide conversion*—After ^{233}Pa removal, the aqueous solution of neptunium in nitric acid is transferred to a glovebox facility. Ammonium nitrate is added to the solution as part of the feed adjustment. The solution containing neptunium is then denitrated in a rotary kiln to convert the neptunium nitrate to an oxide (NpO_2) in a process called “modified direct denitration.” This process was originally developed to convert uranium nitrate to an oxide. At the beginning of the Plutonium-238 Supply Project, ORNL tested and made changes to the existing modified direct denitration process to allow production of NpO_2. The modified direct denitration process was then scaled up to a rate of 80–100 g/h of NpO_2, which is the expected scale for full-scale production operations. The unit has been in place and working since 2013, although it is currently only operated in ~200 g batches because of limits on target fabrication rate. Additional scale up of target fabrication is expected during 2021-2023.

4. OPTIMIZATION

ORNL is also in the process of optimizing the overall flowsheet to increase the production rate and decrease unit costs. Two major efforts started in 2016.

(1) Modified target design—A target containing only NpO_2 pellets encapsulated in a Zircaloy-clad is being tested. This target design has the potential to increase ^{238}Pu production, decrease the number of targets required for irradiation, and eliminate the need for aluminum dissolution.

(2) Enhanced chemical processing—A model of material flows throughout the entire process was developed to identify bottlenecks. Aluminum dissolution was identified as a major bottleneck. Successful completion of the modified target design described above should increase production and decrease unit costs. Additional process bottlenecks will be identified as data are developed. The model will be used to optimize production by increasing yield and decreasing unit costs.

5. SUMMARY

ORNL has reestablished the nation’s capability to produce ^{238}Pu. Interim production operations are underway to fabricate and irradiate targets and to conduct chemical separations for neptunium/plutonium recovery and purification. The current status of activities is listed below:

- Target fabrication has been scaled up to production targets.
- Aluminum and actinide dissolution steps have been successfully demonstrated.
- Solvent extraction separations on material from irradiated targets occurred in late 2018 and provided a baseline flowsheet.
- Laboratory tests of cation exchange separations have been successful in removing large quantities of Np from the Pu product. This process step has been incorporated into Np preparations.
- Anion exchange purification of neptunium solutions has been completed for the first production campaign.

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REFERENCES

[1] T. TODD, R. HERBST, B. MINCHER, S. FRANK, J. LAW, and J. SWANSON, “Plutonium-238 Recovery from Irradiated Neptunium Targets Using Solvent Extraction,” INL/CON-06-11850, Idaho National Laboratory Report (October 2006).

[2] Committee on the Planetary Science Decadal Survey, National Research Council, “Vision and Voyages for Planetary Science in the Decade 2013–2022,” National Academies Press, Washington, (2011).

[3] G. H. THOMPSON and M. C. THOMPSON. “Solvent Extraction of Irradiated Neptunium Targets. I. Valence Stabilization,” DP-1452, Savannah River Laboratory (1977).

[4] G. H. THOMPSON and M. C. THOMPSON. “Solvent Extraction of Irradiated Neptunium Targets. II. Valence Stabilization,” DP-1460, Savannah River Laboratory Report (1977).