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Oak Ridge National Laboratory Preparation of Sintered $^{237}NpO_2$ Pellets for Irradiation to Produce ^{238}Pu Oxide

R.J. Vedder

September 2018

OAK RIDGE NATIONAL LABORATORY
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Nuclear Security and Isotope Technology

OAK RIDGE NATIONAL LABORATORY PREPARATION OF SINTERED $^{237}NpO_2$ PELLETS FOR IRRADIATION TO PRODUCE ^{238}Pu OXIDE

R.J. Vedder

September 2018

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ACRONYMS

DSC	Differential Scanning Calorimetry
HFIR	High Flux Isotope Reactor
MDD	modified direct denitration
ORNL	Oak Ridge National Laboratory
REDC	Radiochemical Engineering Development Center
RPSs	Radioisotope Power Systems
SRS	Savannah River Site
TD	theoretical density
TGA	Thermogravimetric analysis

ABSTRACT

The reference flowsheet for the production of plutonium-238 (^{238}Pu) is by irradiation of targets containing pellets that have been cold-pressed from a mixture of NpO_2 and Al powders and are referred to as cermet pellets or compacts. Oxide pellets, cold-pressed from NpO_2, are being considered because reactor physics and thermal-hydraulic analyses showed that going to 100% oxide decreases the number of pellets that must be pressed and the number of targets that must be fabricated, transported to and from the reactors, irradiated, and processed to recover the production goals of high-purity PuO_2 [85% ^{238}Pu (isotopic purity)]. In addition, elimination of the aluminum constituent has significant waste minimization advantages in a production operation. Details of a fabrication method to make NpO_2 pellets, from preparation of neptunium oxide powder through sintering of the pressed pellets, are given. Pellets of the required density and tight dimensional tolerance were prepared for the fabrication of test targets and have completed irradiation at the Oak Ridge National Laboratory High Flux Isotope Reactor. This work is part of the effort to reestablish domestic production of ^{238}Pu for the National Aeronautics and Space Administration and the US Department of Energy.

1. INTRODUCTION

The National Aeronautics and Space Administration and the US Department of Energy have been tasked to reestablish a program for the domestic production of plutonium-238 (^{238}Pu) formerly produced at the Savannah River Site (SRS).[1] ^{238}Pu is produced in a nuclear reactor from the irradiation of neptunium-237 (^{237}Np) target material and is used for the fabrication of Radioisotope Power Systems (RPSs). RPSs, powered by ^{238}Pu decay heat, are the established power source technology for space missions where solar power is not viable. One type of irradiation target being tested at Oak Ridge National Laboratory (ORNL) contains stacked oxide pellets (sintered NpO_2) similar to typical nuclear reactor fuel (sintered UO_2) pellets. The entire pellet fabrication process, from preparation of pellet-press oxide through final pellet dimensional measurements and assembly of irradiation targets, is performed in a series of gloveboxes at ORNL's Radiochemical Engineering Development Center (REDC). Details of a fabrication process to make NpO_2 pellets, from preparation of neptunium oxide powder through sintering of the pressed pellets, are given. Pellets of the required density and tight dimensional tolerance were prepared for fabrication of test targets that have completed 3 cycles of irradiation at ORNL's High Flux Isotope Reactor (HFIR) and awaiting transfer for post-irradiation examination. Because the green pellets undergo significant handling, high physical integrity was also required to avoid chipping and cracking.

The reference flowsheet calls for the production of ^{238}Pu by irradiation of targets containing ceramic-metallic (cermet) NpO_2–aluminum (Al) pellets, which are also referred to as compacts. Several thousand cermet pellets have been made, assembled into targets, and successfully irradiated to produce ^{238}Pu. Oxide pellets are being considered because reactor physics and thermal-hydraulic analyses showed that going to 100% oxide decreases the number of pellets that must be pressed and the number of targets that must be fabricated, transported to and from the reactors, irradiated, and processed to recover the production goals of high-purity PuO_2 [85% ^{238}Pu (isotopic purity)]. In addition, elimination of the aluminum constituent has significant waste minimization advantages in a production operation.

During irradiation of targets containing cermet pellets approximately 20% of the ^{237}Np is converted to ^{238}Pu, which leaves approximately 80% as a recycle stream. Conversion may be lower for oxide pellets. Irradiated targets are processed in the REDC cell bank to produce a purified neptunium nitrate solution in addition to the plutonium product stream. Makeup neptunium is obtained from an inventory of NpO_2 that originated from SRS. Oxide is dissolved in the REDC hot cells, and the neptunium nitrate solution is concentrated by evaporation. To date, the two streams—recycle and makeup—have been kept separate, and acceptable cermet pellets have been made from each. Oxide pellets of acceptable dimensions and density have been prepared only from solutions originating from the dissolution of stored SRS oxide.

Immediately prior to transfer from the cell bank, the neptunium nitrate solution is passed through a column containing silica gel or porous glass beads to remove the gamma-emitting daughter of ^{237}Np, protactinum-233 (^{233}Pa).[2] The equipment used for converting the neptunium nitrate solution to oxide and preparing the pellets is contained lightly shielded gloveboxes. The removal of ^{233}Pa provides a few weeks to work with the neptunium in the gloveboxes before ^{233}Pa ingrowth becomes a dose of concern to glovebox workers.

Pellets prepared for irradiation are cold pressed from powder using a uniaxial press. Characteristics of the powder produced can be controlled to some extent by controlling the conditions under which the oxide is prepared. The goal is to consistently produce feedstock with acceptable characteristics. Additionally, the time for ingrowth of ^{233}Pa is minimized since conversion of the originating neptunium nitrate solution to pellet–press oxide can be performed within a few days of receipt of the solution. A process developed at ORNL in the 1980s is used to prepare NpO_2 powder to make irradiation pellets. The process, Modified Direct Denitration[3–7](MDD), uses ammonium nitrate to alter the thermal decomposition behavior of metal nitrates and to simplify preparation and improve the ceramic properties of the resulting oxide. Direct thermal conversion is considered the simplest method for making metal oxides from a starting metal nitrate solution; however, oxide prepared by standard direct thermal denitration produces oxide with characteristics and that are unsuitable for making oxide pellets without significant mechanical working. MDD has been examined for conversion of uranium, plutonium, and mixed uranium/plutonium nitrate solutions[8] but not neptunium nitrate. Because neptunium nitrate forms a compound similar to uranium and plutonium with ammonium nitrate [e.g., $(NH_4)_2Np(NO_3)_6$], MDD conversion was considered possible.

As developed, MDD is a continuous process, employing a rotary kiln. Initial tests prepared NpO_2 batch-wise using a stainless steel beaker heated on a hot plate since this technique has been successfully employed to evaluate whether a given metal nitrate solution can be processed by MDD. Physical properties of batch products are reasonably close to those of the continuously produced oxide. More significantly, decomposition of the nitrate salt can be observed to evaluate the suitability of processing with a rotary kiln. Following MDD conversion, batch products were heated to make dense, low-surface-area powder typically used to prepare cermet pellets, and NpO_2–Al compacts were made. Initially no oxide pellets were made. The results were positive, so the decision was made to proceed with installing the equipment into two new gloveboxes for a continuous MDD conversion operation. Existing gloveboxes contain standard powder characterization equipment for measurement of tap density, B.E.T. surface area, particle size distribution, and an X-ray diffractometer, which was used to identify the oxide of neptunium that was made.

The conversion equipment is contained in two HEPA–filtered air–atmosphere gloveboxes, as shown in Figure 1. There are differences between the equipment developed in the original work (described in Reference 3) and what we used. The primary difference is that the two rods internal to the rotary kiln heated pipe rolled freely in the original process, whereas we used two rods that are pinned to the tube that runs through the centerline of the rotary kiln (referred to as the center tube). The roller rods are required to break up the agglomerating decomposing nitrate salt into a flowable powder that is uniformly heated. Our work with a fume-hood version of the equipment found that unpinned roller rods would stick to the retaining plate/disk and simply rotate with the heated pipe, rendering them ineffective. The rotary kiln heated pipe internals used for neptunium nitrate conversion are shown in Figure 2. This design incorporates the following:

1. multiple roller rods (as previous versions) to break up agglomerates;

2. a 1/8 in. ID thin-wall stainless steel tube inside the center tube through which feed solution is pumped and which drips onto the heated pipe through holes in the bottom of the center tube;

3. a scraper bar to limit the amount of material that can accumulate on the heated pipe;

4. prevention of the roller rods from pivoting on the retainer disk and simply rotating with the heated pipe;

5. holes in the top and side of the tube for removal of off-gas (decomposition gases and steam) and holes in the bottom for the feed solution to drip into the rotating heated pipe (as previous versions); and

6. a stainless steel sheathed three-point thermocouple inserted into the center tube from the product end to permit monitoring the heated pipe centerline temperature at the feed addition point and two locations downstream (as previous versions).

Additionally, an off-gas vent connected to the rotary kiln entrance hood to supplement off-gas removal performed by the center tube was added. This provides ventilation for the rotary kiln heated pipe outside the region where powder is produced. Off-gas vapors that condense in the entrance hood are collected in a vacuum flask and are recycled at the beginning of a subsequent conversion run.

Figure 1. Glovebox contained MDD process equipment (feed/scrubber systems in left glovebox rotary kiln and product collection in right glovebox).

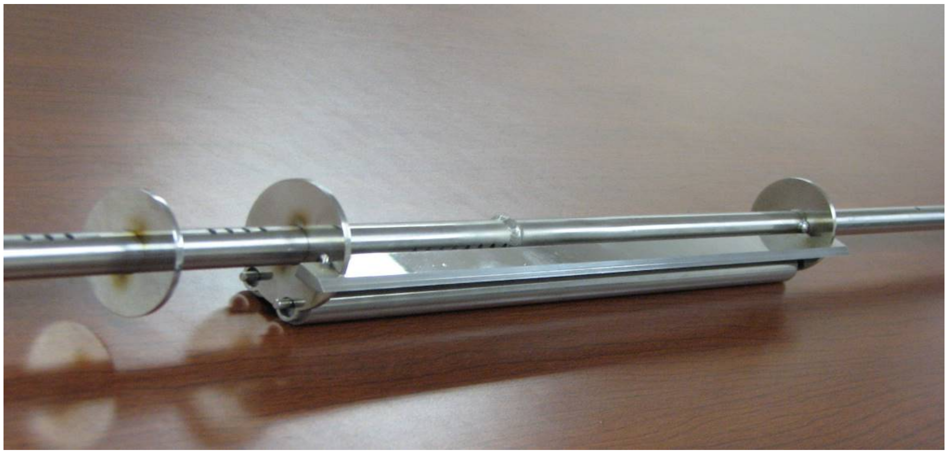


Figure 2. Heated pipe internals with scraper bar and pinned roller rods.

A conversion run begins with heating up the furnace concurrently with rotation of the heated pipe. The ancillary systems vacuum, cooling water, off-gas scrubber, etc., are started. Also included is the air purge, which enters the kiln from the product side and serves to keep off-gas away from the product and direct decomposition gases out of the heated pipe. When the heated pipe reaches steady-state heat-up temperature, water begins to be added. The purpose is to cool the feed tube sufficiently to prevent feed from decomposing inside the line. After a short while, feed addition begins and then the operating conditions, such as feed rate, vacuum, and centerline temperature near the feed point, are monitored. The product is collected in a clear polycarbonate bottle, which permits the rate of accumulation to be observed.

Operating variables were examined in the initial conversion runs. Operating conditions for preparing NpO_2 that is suitable for making either cermet or oxide pellets are as follows:

- Feed solution neptunium concentration: ~200 g/L (range of 150 to 225 g/L)
- Ammonium (modifier)–to–neptunium mole ratio: 2.5:1 (range of 2.2:1 to 3.5:1)
- Modifier by addition of ammonium nitrate salt or reaction of ammonium hydroxide with solution nitric acid
- Countercurrent air purge rate: ~8 scfh
- Heated tube rotation speed: ~10 rpm
- Furnace controller setpoints: 675°C max for both heating zones of the two-zone furnace
- Angle of incline: 10 degrees
- Feed addition rate: 3.5 to 5.5 mL/min

The rotary kiln was fabricated by the Mellen Company and has a 304L stainless steel rotating tube of 2-3/8 in. ID that is heated over 10 in. of its length by an electrical two-zone furnace capable of operating at 1200°C. The production rate is ~80 g/hr of Np_3O_8 at a feed concentration of 200 g Np/L More than 8 kg of neptunium has been processed via MDD without encountering any significant operational problems.

2. HEAT TREATMENT TO CONVERT Np_3O_8 TO NpO_2 AND PREPARE PELLET-PRESS OXIDE

The equipment used to convert neptunium nitrate solution to NpO_2 powder to make either cermet or oxide pellets is the same. The primary difference in preparation is the post-conversion heating temperature. For oxide pellets, a sinterable powder of relatively large surface area and small particle size (see Reference 3) is preferred. Additionally, after pressing into a pellet, the oxide should not undergo a chemical change during subsequent sintering. For cermet pellets, a dense oxide of low surface area and large particle size is preferred for the ceramic component. The maximum operating temperature of the rotary kiln is constrained by materials of construction and is too low to make NpO_2. The higher oxide of neptunium, identified by x-ray diffraction as Np_3O_8 or Np_2O_7, is converted to NpO_2 prior to pressing into pellets. Using batch heating in air, the higher oxide is fully converted to NpO_2 after 2 hr at 620°C. The upper constraint on post-conversion heating temperature in making oxide pellets is that the oxide must be sufficiently sinterable that the pressed pellets densify during sintering. A flowsheet of the post-conversion powder processing steps and preparation of sintered NpO_2 pellets is shown in Figure 3. The first two sieving steps employ ½ in. diameter zirconia grinding media.

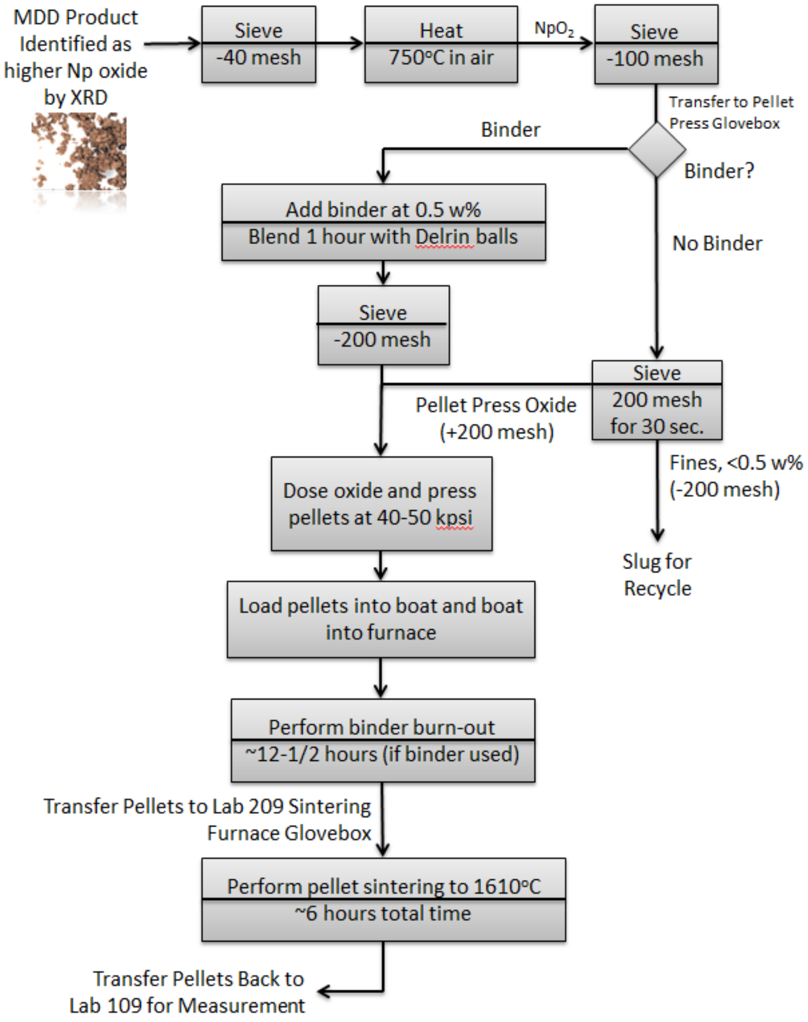


Figure 3. Steps for preparation of sintered NpO_2 pellets from MDD product.

For the powders made, existing glovebox-contained instruments were used to measure standard powder characteristics: tap density using a Quantachrome AutoTap; B.E.T. surface area using a Belsorp Mini analyzer; and particle size distribution using a Microtrac S3500 light scattering analyzer. Additionally, a Rigaku Miniflex II X-ray diffractometer producing CuKα x-rays was used for compound identification (JADE software), and a Leica stereomicroscope was used to examine the morphology of the powders and to examine the surface of pressed pellets. Typical properties of pellet-press NpO_2 are given in Table 1. The particles are irregularly shaped agglomerates whose measured size distribution depends upon sample preparation, which was the same for all samples. The significantly lower surface area and larger particle size of the cermet oxide indicated that the oxide had sintered to some extent. Following batch heating to prepare pellet oxide, the 635 and 750°C heated products were flowable powders while the cermet oxide was a porous mass formed by the crucible.

Table 1. Typical NpO_2 powder characteristics.[a]

Post-conversion heating temperature, ˚C	Tap density, g/mL	B.E.T. specific surface area, m^2/g	Particle size distribution, µm		
			d10[b]	d50[c]	d90
1185	3.8	0.2	0.4	2.7	7.6
750	2.8	2.7	0.2	0.7	4.4
635	2.6	3.8	NM[d]	NM[d]	NM[d]

[a] Modifier ratio of 2.5 mol NH_4: 1 mol Np

[b] Percentage (10, 50, and 90) of particles that are smaller than the indicated size, diameter for sphere of same volume

[c] Commonly reported median particle diameter

[d] Not measured

An image of NpO_2 used to prepare oxide pellets taken at a magnification of 100× is shown in Figure 4. The oxide appears to be agglomerates of smaller irregularly shaped particles similar to UO_3 produced by MDD.

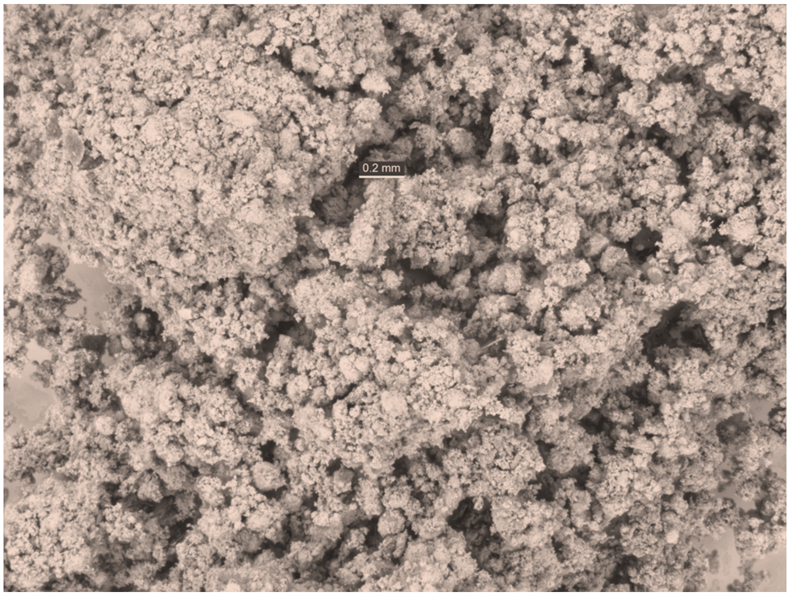


Figure 4. Image of heated (750°C) and sieved NpO_2.

3. NEPTUNIUM OXIDE PELLET DEVELOPMENT

Existing equipment used to prepare NpO_2-Al cermet pellets was used to develop a preparation technique for making oxide pellets. The fully sintered oxide pellets are of larger diameter (~0.325 in.) than the cermet pellets (~0.250 in.), but cermet die sets were initially used for the sake of simplicity and to lessen the amount of neptunium required. (Each full-size oxide pellet has greater than four times the mass of neptunium of a cermet pellet.) The need to modify the cermet pellet-die by adding a taper at the exit to prevent pellet lamination (radial breaking of a pellet into several "small pellets") was quickly recognized. Dies used to make oxide pellets typically have a taper of ½ to 2 degrees over a ¼ in. length at the pellet exit[8] for the pellet to expand gradually as it exits the die. This modification essentially eliminated pellets sectioning on ejection. The same modification was made to commercially available 10 mm dies purchased from MTI Corp. that were subsequently used to make full-size oxide pellets (Figure 5). No other equipment used to produce cermet pellets was modified.

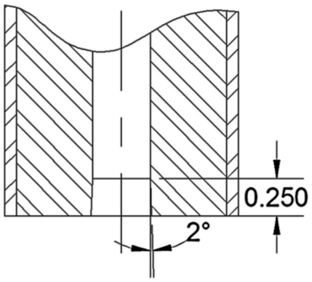


Figure 5. Modified commercial die.

For initial irradiation tests, the objective was to make pellets of uniform diameter and of density 90+% of theoretical. The dimensional requirement was necessitated by the current inability to machine oxide pellets, typically done with a centerless grinder, to a single diameter. Irradiation test pellets (four per target initially) were grouped based upon diameter to ensure an acceptably tight fit with the machined ID cladding tube. The gap, filled with helium gas, is a significant thermal resistance.

Variables examined in preparing NpO_2 pellets were as follows:

1. MDD conversion conditions—two conditions for preparing pellet–press oxide were examined;
2. post-MDD–conversion product heating—two temperatures were examined to produce an acceptably dense powder that is sufficiently active to produce sintered NpO_2 pellets of minimum 90% theoretical density (TD);
3. slugging (pre-compaction to ~50% TD followed by passing through a sieve) to increase pellet-press oxide density;
4. binder/lubricant (four were examined) and technique for mixing with powder; binder evaluation was performed making pellets of cerium dioxide (CeO_2) prepared by MDD conversion of cerium nitrate solution;
5. binder/oxide blending; blending tests were performed in the glovebox with NpO_2;
6. binder concentration and binder burnout, i.e., decomposition of binder from a pressed pellet by heating the pressed pellet at a controlled rate;
7. pellet pressing force;
8. pellet length-to-diameter (l:d) ratio; and
9. pellet sintering temperature profile.

Pellets as-pressed, called green pellets, and following sintering were evaluated as follows:

1. dimensionally using a Mitutoyo laser micrometer and automatic length gage;
2. structural integrity and surface features using a Leica stereomicroscope; and

3. immersion in ethanol or water for density measurement using a Mettler Toledo density kit combined with an existing scale.

Cermet dies which had been modified to have a tapered exit were initially used. At this stage of the development effort, pellet heating (partial sintering) was limited to 1185˚C, the maximum operating temperature of an existing glovebox-contained furnace. This configuration permitted evaluation of several of the variables listed above. Concurrent with the initial pellet development effort, a new glovebox with a furnace capable of operating at ~1610˚C was being installed to permit full sintering of oxide pellets.

3.1 MDD CONVERSION CONDITIONS

Evaluation of preparation conditions of cermet oxide, i.e., MDD product heated to 1185˚C, found a significant increase in density as the modifier concentration was increased. No such impact was found upon heating the MDD product to the lower temperatures required to prepare ceramic pellets. Additionally, no significant impact on either green pellet density or the density of partially sintered oxide pellets was found. The conversion conditions selected for preparing NpO_2 for pressing into oxide pellets were the same as cermet pellets, thus permitting the MDD product to be used for preparing either type of pellet. Not examined extensively, but likely how the modifier is added to the neptunium nitrate solution, whether by addition of ammonium hydroxide to react with nitric acid to form ammonium nitrate or by addition of the salt, may produce a denser, more granular oxide.

3.2 POST-MDD CONVERSION PRODUCT HEATING TEMPERATURE

The MDD product is passed through a 40-mesh screen, poured into zirconia crucibles to a powder depth of approximately 1 in., and heated at the target temperature for 2 hr in air. Two temperatures were examined to prepare NpO_2 for making oxide pellets: 635 and 750˚C.

As expected, the green pellet density was greater (~2% TD) for pellets pressed from the higher-fired oxide. The density of partially sintered pellets (heated to 1185˚C) was also higher, by ~1.5% TD; this was true for all combinations of binder and press pressure. The higher-fired oxide was used to prepare the initial fully sintered irradiation pellets. Post-conversion heating temperature with fully sintered pellets is worth examining further since, based on accepted characteristics, the lower temperature oxide should be more sinterable and thus produce higher density pellets.

3.3 OXIDE SLUGGING OR PRE-COMPACTION

Powders are often slugged to increase bulk/tap density and to improve flow characteristics. Oxide prepared by MDD flows well with little dusting, so the potential benefit was an increase in pellet density. Slugging involves compaction of a relatively large amount of powder, equivalent to several pellets, followed by sieving using grinding media to break up the pellet and pass the powder through a sieve. This adds steps to the pellet preparation sequence. Slugging pellet–press NpO_2 was found to increase powder density but actually decreased the density of partially sintered pellets. Previous work making UO_2 pellets found that significant mechanical working, such as milling, of MDD oxide actually decreased the sinterability of the oxide.[9] Possibly the mechanical working of the powder inherent with slugging was equivalent to milling. Failure to increase pellet density following partial sintering while significantly increasing the pellet fabrication effort eliminated powder slugging as a method for increasing pellet density.

3.4 BINDER SELECTION

Oxides are typically blended with an organic a binder to increase the strength of a pressed (i.e., green) pellet and to act as a lubricant during compaction. In our case, complete removal of the binder must occur while heating in air or under vacuum. Organic binders that thermally decompose to water and CO_2 were examined. Binder evaluation was performed using CeO_2 as a nonradioactive surrogate for NpO_2. The CeO_2 used in the tests was produced from cerium nitrate using the same method employed to produce NpO_2 from neptunium nitrate in the production process. Post-conversion heating and sieving were performed to match important properties of the CeO_2 to NpO_2: bulk density, surface area, and average fundamental particle size. Matching the high density of NpO_2 is not possible, but for examining lubrication properties, green pellet handling strength, and removal of the binder, this is not considered a significant shortcoming. A die with a tapered exit was used to prepare ~0.25 in. diameter green pellets.

For binder removal, or burnout, the temperatures at which the various stages of decomposition occur are first identified. This is typically done by determining weight loss as a function of temperature by thermogravimetric analysis (TGA) and temperatures of thermal events, such as melting by differential scanning calorimetry (DSC). A heating profile is then developed in which the furnace temperature is increased slowly as a reaction temperature is approached and held at that temperature until no additional change is observed. Decomposition temperatures for common binders are published, often by the manufacturer, but hold time and temperature ramp rate must be determined experimentally because they depend upon characteristics of the specific compact. Thermal properties impact the time required to reach uniform temperature throughout the pellet, and porosity impacts removal of decomposition gases (water and CO_2).

Four binders were examined: Carbowax PEG 8000, Stearic/Palmitic Acid mix, Duramax B-1022, and CrystalCer X. The latter two are liquid binders. Initially, 24 pellets were pressed, six pellets using each of the four binders. Binder was added at 1 w% to CeO_2, and the mix was then tumbled for 2 hr to ensure uniform mixing of the binder throughout the oxide. A general binder-removal heating cycle was developed based upon TGA/DSC results for binder decomposition in air. Pellets that were successfully pressed and sintered at 1675˚C for 2 hr in air were examined for physical defects such as cracks, chips, and holes; additionally, pellet density was determined using volume calculated from dimensions taken with a caliper.

Blending the liquid binders (CrystalCer X and Duramax B-1022) with powder was more difficult than with solid binders using the simple blending technique available in the glovebox–a milling tumbler. The liquid binders also produced a coating on the internal surface of the container. Pellets pressed with the Duramax B-1022 binder failed upon pellet ejection. Sintered pellets prepared with CrystalCer X had large surface holes likely caused by poor blending with powder and were of lower density, using geometrical volume, than pellets pressed with solid binders.

The two solid binders performed equally well in test-pressings with surrogate oxide and were selected for additional testing by pressing and partial sintering of 0.25 in. diameter NpO_2 pellets. The results of these tests found no significant difference between the binders in terms of green pellet strength, binder decomposition, and pellet density following heating to 1185°C. A pellet density of ~85% of theoretical was achieved with pellets pressed from both binders. For simplicity, the binder selected was a stearic/palmitic acid mixture since it, in acetone solution, is used as the die lubricant for both cermet and oxide pellets.

3.5 BINDER/OXIDE BLENDING

A binder is typically employed in cold-pressing oxide powder in order for pellets of sufficient strength to remain intact during ejection from the die and subsequent handling. Initially the same technique used to mix NpO_2 with aluminum powder to make cermet pellets was tried. This involved simply tumbling the two components for 30 minutes. Oxide pellets prepared from this blend following partial sintering to 1185°C had large voids visible on the pellet surface. Examination of the mix, shown in Figure 6, revealed large agglomerates of binder coated with oxide which, following binder decomposition, left voids in a pellet too large to fill by sintering.

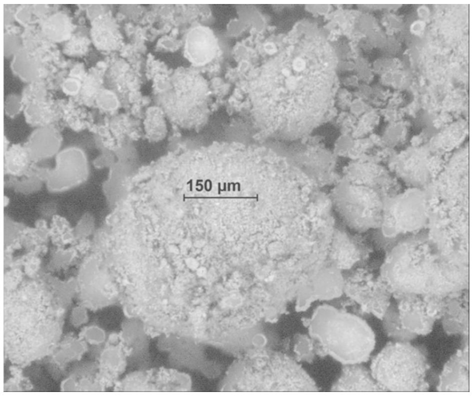


Figure 6. Mixture of NpO_2 and stearic:palmitic acids binder after simple tumbling.

A blending technique that resulted in acceptably small agglomerates was developed.[10] Delrin spheres were added to the oxide and the mix and tumbled for 1 hr. The mix was then passed through a 200-mesh screen.

3.6 BINDER CONCENTRATIONS AND POST-PRESSING BURNOUT

Decomposition characteristics of the two binders evaluated for preparing NpO_2 pellets are given in Table 2. Complete decomposition with no residue, i.e., weight gain, when heating in air was shown by TGA. The melting point was determined by DSC.

Table 2. TGA/DSC of binders.[a]

Binder/solid lubricant	Melting temperature, ˚C	Decomposition temperature range, ˚C
PEG (Carbowax 8000)	67	Primary: 190 to 350, complete by 525
~50:50 w% stearic:palmitic acids	61	Primary: 175 to 325, complete by 525

[a] Results provided by Fred Montgomery of ORNL.

Following pressing, green pellets were heated to remove (decompose to water and carbon dioxide) the binder. The information given in Table 2 was used to develop a heating profile. The heating profile found to produce acceptable visible/surface porosity is given in Figure 7. More rapid heating (~6 hr) produced pellets having what are called “blowholes,” as shown in Figure 8. The numerous large pores also indicated poor mixing of the binder with oxide, as discussed in the previous section.

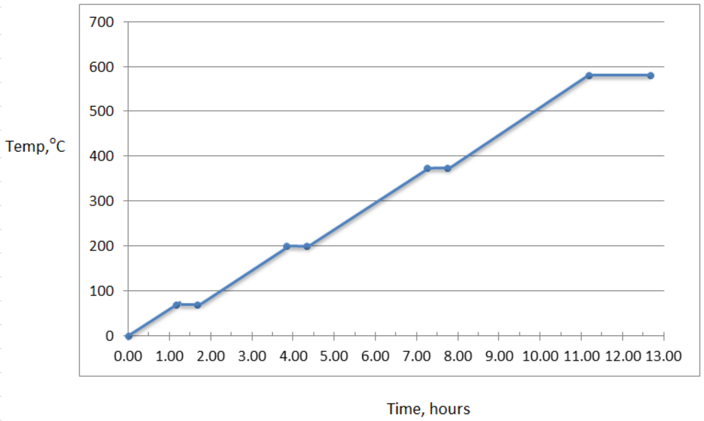


Figure 7. Binder burnout temperature ramping program.

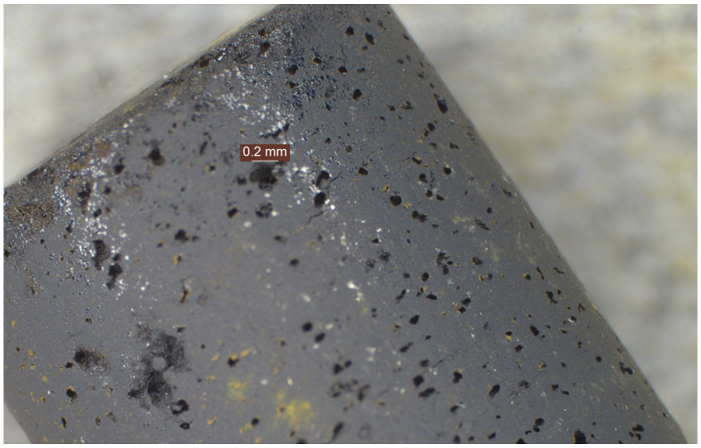


Figure 8. Surface of pellet with binder burnout indicating excessively rapid heating rate and poor binder/oxide blending.

Pellets were pressed with binder concentrations between 4 wt% and 0.5 wt%; additionally, pellets were successfully pressed and sintered without a binder. Partial and fully sintered pellet density increased significantly as the binder concentration decreased. Ideally, oxide pellets are pressed without a binder since this eliminates the blending and sieving steps and reduces binder decomposition time to that required to remove/decompose a pellet surface lubricant.

3.7 PELLET PRESS FORCE

Compaction pressures given in Table 3 were examined initially for preparing 0.25 in. diameter pellets and subsequently full-size pellets. The sintered (or partially sintered) density for full-size pellets was slightly higher than that for the smaller pellets pressed at the same force at the same length-to-diameter aspect ratio.

The lowest two press pressures were eliminated because of low green and thus sintered pellet density. Green pellet density at higher pressures averaged ~50% of theoretical for pellets of 0.75 aspect ratio.

Table 3. Compaction pressures examined.

Variable ID	Pressure, lb/in^2	For 0.25 in. die press force, lb$_f$	For 10 mm die press force, lb$_f$
P1	32,000	1600	4000
P2	50,000	2450	6100
P3	22,000	1100	2700
P4	19,000	950	2325
P5	40,000	2000	5000
P6	45,000	2250	5520

In the range of 32 to 50 kpsi, the sintered pellet density increased as the pressing force increased for a typical set of conditions, as shown in Figure 9. Lamination occurred with some pellets pressed at 50 kpsi; this was not observed at pressures P5 or P6.

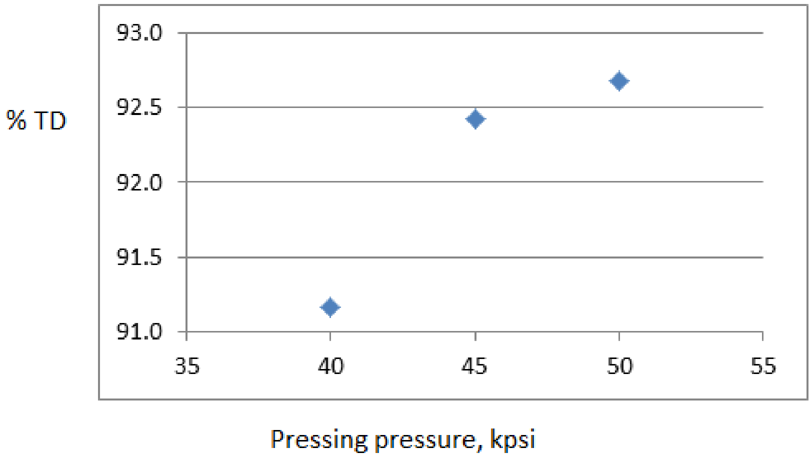


Figure 9. Compaction pressure effect on sintered pellet density.

3.8 PELLET LENGTH: DIAMETER RATIO

The effect of l:d ratio on sintered pellet density was examined by pressing pellets of varying mass oxide prepared identically and the sintered pellets prepared under the same conditions. A significant increase in the density of sintered pellets was found as l:d was decreased from 1.0 to 0.75. Sintered pellet density increased from ~90% TD to ~93% TD. No significant impact on pellet dimensional uniformity was observed. Pellet diameter was constrained during the development work by commercially available die sets and the ID of irradiation test targets; obviously, decreasing pellet length by decreasing the mass of NpO_2 per pellet would increase the number of pellets needing to be made.

Typical pellet geometry is 1:1 using a biaxial press in which the press force is exerted on both the top and bottom of the oxide inside the die. We were constrained to using a uniaxial press in which the press force was exerted from only the top of the die and the pellet ejected through the bottom. Application of quasi-dual-action pressing in which a spring is used to exert a force on the bottom of the die/plug assembly which floats was found to be impractical.

In order to consistently achieve a sintered pellet density of 90% of theoretical or higher and uniform diameter using a uniaxial press, a l:d ratio of 0.75 was found to be acceptable. Longer pellets were found to have similar diametrical uniformity but lower density. Possibly sintered pellet density could be increased by decreasing the pellet aspect ratio.

3.9 GREEN PELLET SINTERING

The pellet sintering furnace is a Micropyretics Heaters International (MHI) Z-Series Box Furnace operating in air. The furnace is contained inside an air-atmosphere HEPA-filtered glovebox which was installed by this project; thus, the furnace was not available in early development work and green pellet sintering was limited to heating at 1185°C. The location and furnace design place constraints on the operation: a temperature limit of 1615°C and a hold time at temperature of 3-1/2 hr.

Initially a very slow ramp rate of 1.6°C/min, common for sintering oxide pellets, was used but heating elements failed after one or two heatings. Likely the constant cycling of power by the controller during initial slow ramping caused the elements to fail. The heating profile was then changed to essentially the conditioning profile recommended for new heating elements, and no subsequent element failures have been experienced. The sintering program ramps to 1600°C at 10°C/min, holds for 3 to 3-1/2 hr, ramps down to 800°C at 8°C/min, and then steps down to 0°C.

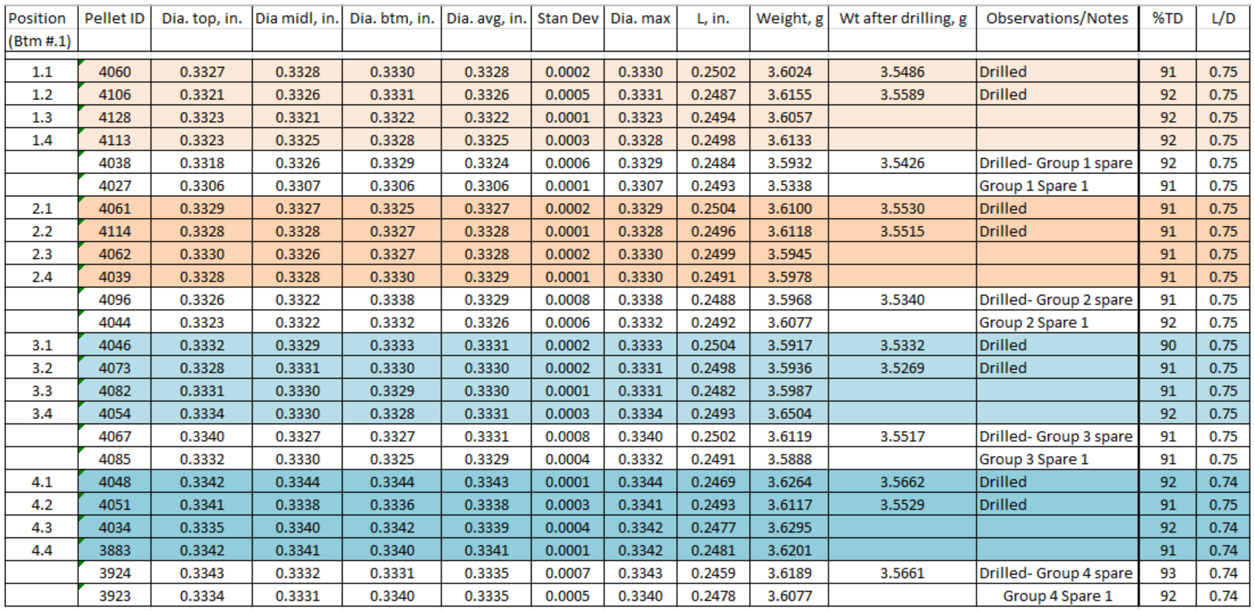
4. SINTERED NEPTUNIUM DIOXIDE IRRADIATION TEST PELLETS

Oxide pellets prepared for test irradiation targets detailed in this report originated from MDD conversion of neptunium nitrate solution obtained simply by dissolving stored Savannah River NpO_2. No REDC-processed recycle neptunium was used; cermet pellets, however, have been made with solutions of either origin. Appendix A provides chemical impurity analysis of the originating oxide as transmitted by Savannah River.

Four test targets, each containing four pellets, were prepared for the first irradiation experiment. An excess of pellets was pressed and then grouped based upon sintered pellet diameter. Zircaloy target tubes were drilled for an acceptably tight fit between the pellets and tube inner wall. The bottom two sintered pellets were drilled to accept wires of hafnium metal, which has a lower melting point than NpO_2, as an indication of the proximity of the pellets to melting during irradiation. Drilling was performed using the procedure given in Appendix B. Pellets were prepared under conditions of varying force and binder concentration (0, 0.5, and 1 w% binder), which led to variations in density. Pellet dimensional and target loading information is given in Table 4. Because of difficulties associated with operation of the immersion density equipment, pellet density was calculated from geometry, and thus actual pellet densities are higher than those given in Table 4.

The furnace can accommodate three zirconia boats of four pellets each. A boat of pellets following sintering is shown in Figure 10.

Table 4. Pellets selected for irradiation testing.



Position (Btm #.1)	Pellet ID	Dia. top, in.	Dia midl, in.	Dia. btm, in.	Dia. avg, in.	Stan Dev	Dia. max	L, in.	Weight, g	Wt after drilling, g	Observations/Notes	%TD	L/D
1.1	4060	0.3327	0.3328	0.3330	0.3328	0.0002	0.3330	0.2502	3.6024	3.5486	Drilled	91	0.75
1.2	4106	0.3321	0.3326	0.3331	0.3326	0.0005	0.3331	0.2487	3.6155	3.5589	Drilled	92	0.75
1.3	4128	0.3323	0.3321	0.3322	0.3322	0.0001	0.3323	0.2494	3.6057			92	0.75
1.4	4113	0.3323	0.3325	0.3328	0.3325	0.0003	0.3328	0.2498	3.6133			92	0.75
	4038	0.3318	0.3326	0.3329	0.3324	0.0006	0.3329	0.2484	3.5932	3.5426	Drilled- Group 1 spare	92	0.75
	4027	0.3306	0.3307	0.3306	0.3306	0.0001	0.3307	0.2493	3.5338		Group 1 Spare 1	91	0.75
2.1	4061	0.3329	0.3327	0.3325	0.3327	0.0002	0.3329	0.2504	3.6100	3.5530	Drilled	91	0.75
2.2	4114	0.3328	0.3328	0.3327	0.3328	0.0001	0.3328	0.2496	3.6118	3.5515	Drilled	91	0.75
2.3	4062	0.3330	0.3326	0.3327	0.3328	0.0002	0.3330	0.2499	3.5945			91	0.75
2.4	4039	0.3328	0.3328	0.3330	0.3329	0.0001	0.3330	0.2491	3.5978			91	0.75
	4096	0.3326	0.3322	0.3338	0.3329	0.0008	0.3338	0.2488	3.5968	3.5340	Drilled- Group 2 spare	91	0.75
	4044	0.3323	0.3322	0.3332	0.3326	0.0006	0.3332	0.2492	3.6077		Group 2 Spare 1	92	0.75
3.1	4046	0.3332	0.3329	0.3333	0.3331	0.0002	0.3333	0.2504	3.5917	3.5332	Drilled	90	0.75
3.2	4073	0.3328	0.3331	0.3330	0.3330	0.0002	0.3331	0.2498	3.5936	3.5269	Drilled	91	0.75
3.3	4082	0.3331	0.3330	0.3329	0.3330	0.0001	0.3331	0.2482	3.5987			91	0.75
3.4	4054	0.3334	0.3330	0.3328	0.3331	0.0003	0.3334	0.2493	3.6504			92	0.75
	4067	0.3340	0.3327	0.3327	0.3331	0.0008	0.3340	0.2502	3.6119	3.5517	Drilled- Group 3 spare	91	0.75
	4085	0.3332	0.3330	0.3325	0.3329	0.0004	0.3332	0.2491	3.5888		Group 3 Spare 1	91	0.75
4.1	4048	0.3342	0.3344	0.3344	0.3343	0.0001	0.3344	0.2469	3.6264	3.5662	Drilled	92	0.74
4.2	4051	0.3341	0.3338	0.3336	0.3338	0.0003	0.3341	0.2493	3.6117	3.5529	Drilled	91	0.75
4.3	4034	0.3335	0.3340	0.3342	0.3339	0.0004	0.3342	0.2477	3.6295			92	0.74
4.4	3883	0.3342	0.3341	0.3340	0.3341	0.0001	0.3342	0.2481	3.6201			91	0.74
	3924	0.3343	0.3332	0.3331	0.3335	0.0007	0.3343	0.2459	3.6189	3.5661	Drilled- Group 4 spare	93	0.74
	3923	0.3334	0.3331	0.3340	0.3335	0.0005	0.3340	0.2478	3.6077		Group 4 Spare 1	92	0.74

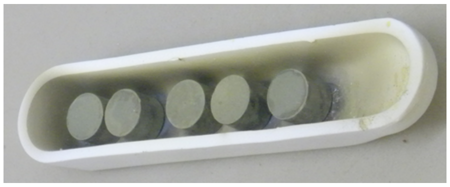


Figure 10. Oxide pellets used in irradiation test targets following full sintering.

5. SUMMARY AND CONCLUSIONS

A method for preparing NpO_2 powder for cold pressing into either cermet or oxide pellets was developed. Starting with neptunium nitrate solution, NpO_2 is produced by Modified Direct Denitration, which following batch heating in air produces NpO_2 suitable for pressing into either type of pellet. The reference flowsheet for the production of ^{238}Pu by irradiation of ^{237}Np uses cermet pellets, but oxide pellets have significant advantages. Conditions for fabricating fully sintered oxide pellets of high density and uniform dimensions were developed, and the first group of targets was prepared for irradiation experiments in HFIR to produce ^{238}Pu. Upon completion of the irradiation cycles, the targets will be transferred to an ORNL hot cell facility to undergo standard post- irradiation examination. Pellets recovered will then be transferred to the REDC hot cells for dissolution, mainly to determine yield and quality of the resulting ^{238}Pu.

The primary variables for making pellets of high density and uniformity are (1) binder concentration, (2) pellet aspect ratio, and (3) pellet press force. Conditions were initially set for the other fabrication variables following testing using a surrogate oxide, pressing pellets smaller than the likely production size, and performing partial sintering prior to installation of a new glovebox containing a sintering furnace.

Recommended conditions for preparing oxide pellets:

1. conversion of neptunium nitrate solution to produce NpO_2 per Section 2;
2. post-conversion heating to 750°C and sieving per the flowsheet in Figure 3;
3. if necessary for pellet integrity, blending of NpO_2 with ~50:50 wt% stearic:palmitic acids as binder per Section 4.5 at a maximum concentration of 0.5 wt%;
4. compaction of 3.66 g of press powder at 45 kpsi to prepare a green pellet of l:d ratio of 0.75 and density ~50% of theoretical;
5. green pellet heating profile per Figure 7 for binder removal or a shorter heating program to remove die lubricant; and
6. green pellet sintering per the heating program given in Section 4.9.

Following fabrication, sintered pellet mass and dimensional measurements will be taken, and the pellets will be visually inspected primarily for excessive end-chipping and cracks.

Additional recommendations for fabricating the next irradiation test pellets:

1. Determination of pellet density by immersion is the standard method used for oxide pellets and is thus preferred over geometrical; hence, use of the Mettler Toledo density instrument should be investigated further.
2. Ideally oxide pellets are pressed without using a binder because of the significant decrease in fabrication time and handling (dose to glovebox workers) and increased sintered pellet density. Five pellets were pressed and sintered without binder, with zero rejects. Pressing pellets without the binder should be the goal for the next round of pellet fabrication.
3. Decreasing the neptunium concentration in the MDD feed to approximately one-half of the standard concentration was found to increase the tap density of cermet oxide. Whether this would have a similar impact on lower-fired oxide and result in an increased density of oxide pellets should be examined.
4. Sintering agents should be used to determine whether lowering the sintering temperature improves pellet solubility in nitric acid.
5. Results from the post-irradiation examination of pellets from the first irradiation will indicate whether the pellet density needs to be increased. The simplest method of achieving this is to make pellets of a lower aspect ratio possibly pressed at a higher force. Better yet would be examination of the final sieving step, possibly use of a coarser powder, since if successful this would not increase the number of pellets needing to be fabricated for an irradiation target.

6. REFERENCES

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APPENDIX A. SAVANNAH RIVER NEPTUNIUM DIOXIDE DISSOLVED TO PROVIDE MDD FEED SOLUTION

A sample report provided by Savannah River Laboratory of stored NpO_2 that is dissolved to provide conversion step feed solution to provide pellet feed powder is given in this appendix.

Element/isotope	Concentration	Units
Neptunium 1	87.73	wt%
Neptunium 2	87.91	wt%
Uranium 1	LT 10	µg U/g Np
Uranium 2	LT 10	µg U/g Np
PU-238	40.2	µg Pu-238/g Np
PU-239	12.9	µg Pu-239/g Np
PU-240	1.7	µg Pu-240/g Np
PU-241	LT 0.1	µg Pu-241/g Np
PU-242	1.3	µg Pu-242/g Np
Total Pu by ICP-MS	56	µg Pu/g Np
Total Pu Alpha by ICP-MS	689	µCi Pu/g Np
SILVER	LT 0.6	µg/g
ALUMINUM	LT 21	µg/g
ARSENIC	LT 0.6	µg/g
BORON	LT 27	µg/g
BARIUM	LT 0.3	µg/g
BERYLLIUM	LT 0.3	µg/g
CALCIUM	LT 62	µg/g
Cadmium	LT 5.6	µg/g
CERIUM	8.4E+01	µg/g
CHROMIUM	1.6E+01	µg/g
COPPER	3.0E+00	µg/g
IRON	7.1E+01	µg/g
GALLIUM	LT 0.1	µg/g
HAFNIUM	LT 0.2	µg/g
MERCURY	LT 11	µg/g

POTASSIUM	LT 60	µg/g
LANTHANUM	3.0E-01	µg/g
LITHIUM	LT 4.8	µg/g
MAGNESIUM	1.7E+01	µg/g
MOLYBDENUM	LT 3.2	µg/g
SODIUM	6.7E+01	µg/g
NIOBIUM	LT 0.6	µg/g
NICKEL	1.0E+01	µg/g
PHOSPHORUS	LT 20	µg/g
LEAD	LT 0.4	µg/g
SULFUR	LT 138	µg/g
SELENIUM	LT 5.6	µg/g
SILICON	N/A	µg/g
TANTALUM	LT 0.6	µg/g
VANADIUM	LT 0.1	µg/g
TUNGSTEN	LT 3.6	µg/g
ZINC	3.5E+00	µg/g
ZIRCONIUM	LT 0.4	µg/g
TH-228	LT 0.1	µg/g
TH-229	LT 0.1	µg/g
TH-230	2.6E+00	µg/g
TH-231	2.0E-01	µg/g
TH-232	2.9E+03	µg/g
AM-241	LT 1.0	µg/g
AM-242	LT 1.0	µg/g
AM/CM-243	LT 1.0	µg/g
CM-244	LT 1.0	µg/g
CM-245	LT 1.0	µg/g
CM-246	LT 1.0	µg/g
CM-247	LT 1.0	µg/g
CM-248	LT 1.0	µg/g
CARBON	1.8E+03	µg/g

APPENDIX B. METHOD FOR DRILLING PELLETS FOR INSERTION OF METAL WIRES

The initial irradiation test targets each contain four sintered NpO_2 pellets. Information to be obtained from post-irradiation examination includes whether any melting of the pellets occurred during irradiation. If no melting is detected, then proximity to melting can be evaluated by examining a wire made of hafnium metal (melting point ~300^{o}C lower than NpO_2) that is inserted into a pellet. Two pellets in each target contained a melt wire. The method chosen to make a cavity for insertion of a melt wire was to drill a slightly oversized hole in sintered pellets using a small drill press located inside a glovebox. The method used is as follows.

- The minimum drill depth is 0.13 in.; drill to 0.18 in. (pellets are ~0.25 in. long). Depending upon pellet density, ~0.072 g of NpO_2 will be removed by drilling. This should be recovered.

- Center the pellet beneath the drill bit visually and tighten the vise. Very slowly advance the drill and "zero" the depth gage.

- Using a pipette, place a few drops of water onto the pellet top surface.

- Start the drill rotation at approximately one-fourth setting. Slowly advance the drill bit while observing the drill depth (a second person can read aloud the current depth).

- Drill to a depth of ~0.1 in. and then slowly back out the drill bit. Add water again to the surface of the pellet and resume/complete drilling.

- After drilling is completed, slowly release the pellet from the vise. Use tweezers, if desired, to move the pellet to a container of demineralized water. Carefully squirt water into the hole to remove loose powder from the pellet cavity and clean the pellet. The drilling NpO_2 fines should be retained for recycle.