

Product Conversion: The Link between Separations and Fuel Fabrication

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Abstract – Several chemical processing flowsheets are under development for the separation and isolation of the actinide, lanthanide, and fission product streams in spent nuclear fuel. The conversion of these product streams to solid forms, typically oxides, is desired for waste disposition and recycle of product fractions back into transmutation fuels or targets. The modified direct denitration (MDD) process developed at Oak Ridge National Laboratory (ORNL) in the 1980s offers significant advantages for the conversion of the spent fuel products to powder form suitable for direct fabrication into recycle fuels. A glove-box-contained MDD system and a fume-hood-contained system have been assembled at ORNL for the purposes of testing the co-conversion of uranium and mixed-actinide products. The current activities are focused on the conversion of the first products from the processing of spent nuclear fuel in the Coupled End-to-End Demonstration currently being conducted at ORNL.

INTRODUCTION

The processing of spent nuclear fuel through the various chemical separations flowsheets generates a number of product and waste streams requiring further treatment for recycle, storage, or disposal. The flowsheets under development for processing spent nuclear fuel separate or isolate the actinides, lanthanides, and fission products into individual streams that require further processing for a final disposition path. Most of the product and waste streams are nitric acid solutions resulting from the back-extraction of selected elements from organic extractants or raffinate solutions containing residual elements for disposal. The product streams require conversion to forms suitable for recycle into fuel or targets. Similar conversion is needed for the waste streams in order to immobilize the radioactive constituents in a solid-matrix waste form for long-term disposal. Several co-precipitation processes are and have been considered for product conversions but these require close control of the precipitation conditions to ensure co-conversion of the different elements, plus more complicated equipment for precipitation-filtration-calcination of the desired product.

In the 1980s, a modification of the direct denitration process was developed [1, 2] at the Oak Ridge National Laboratory (ORNL) to produce a fuel-grade UO_2 form with the desired ceramic properties for direct fabrication into fuel pellets. This development activity not only investigated the chemistry of the product

conversion but also examined the development of equipment to accomplish this conversion to oxide. This work ended after a few years of effort because of changes in the supporting programs. This technology was reintroduced in 2001 in the Advanced Fuel Cycle Initiative (AFCI) as a viable method for conversion of separated uranium product from many of the various separations flowsheets being investigated for the processing of spent nuclear fuel. Work has continued on this process under the Global Nuclear Energy Partnership (GNEP) and in the Coupled End-to-End (CETE) Demonstration at ORNL.

MODIFIED DIRECT DENITRATION DEVELOPMENT

The modified direct denitration (MDD) process was initially focused on the conversion of uranyl nitrate solutions to a uranium oxide product. In the conversion of uranyl nitrate solutions by the direct thermal denitration method, as the solution is evaporated, brown fumes evolve from a syrupy, clear melt boiling in the range of 185 to 195°C. As denitration continues, the melt thickens and then forms a glassy cake, which subsequently cracks into pieces with low surface area. This material does require grinding, ball-milling, calcining, or other such methods to improve the ceramic properties for fuel fabrication. To minimize the formation of this glassy matrix, the process has been performed in fluidized beds or stirred troughs with some success. In the MDD development it was determined that with the addition of an inorganic

salt to the uranyl nitrate solution, a yellow crystalline slurry is formed at $\sim 155^{\circ}\text{C}$. This slurry is converted to relatively dry crystals at 180°C , corresponding to a double salt of uranium nitrate–ammonium nitrate. At 280°C , brown fumes evolve with the formation of a trinitrate uranium salt, which further decomposes to UO_3 at $\sim 350^{\circ}\text{C}$. Further crystallization of the UO_3 occurs at $\sim 550^{\circ}\text{C}$, producing an oxide product with ceramic properties suitable for pellet fabrication. This oxide exhibits ceramic properties comparable to those produced by the more traditional conversion processes mentioned earlier.

Pellet Fabrication from MDD Products

Pellet fabrication of the oxide powders produced during the development of the MDD process was studied [1, 2, 4], and it was determined that excellent-quality pellets could be fabricated from this material. Development of the MDD process continued utilizing larger-scale equipment (1 kg/h), and samples of the oxide powder produced in these studies were compared with oxides produced by other methods [5]. It was determined that pellets with 96% theoretical density were produced using standard fabrication techniques. This work was later extended to the production of mixed-oxide powders [6], $\text{UO}_3\text{-PuO}_2$ (~ 22 wt % Pu). The mixed oxides were produced in small-scale conversion equipment, reduced to UO_2 , pressed, and sintered to yield 95% theoretical dense pellets with good appearance and microstructure.

Equipment Development for MDD

Various types of processing equipment for denitration processes have been evaluated, and some have been used for larger-scale production with low-enrichment uranium feeds. Conversion of spent fuel containing uranium and plutonium could require criticality control and remote operation, which greatly influence the choice of equipment. The continuous rotary kiln with breaker bars appears to be a promising choice for this type of operation. This equipment can be easily operated in a continuous or semicontinuous mode to meet the desired throughput of an industrial facility. This equipment was also believed to be scalable from laboratory-sized equipment to pilot scale to full industrial scale without significant adjustments to operating parameters.

Large-scale rotary kiln units (kilograms per hour) are commercially available, but a smaller test unit (grams per hour) was desired for this work to allow for operation with limited quantities of materials in an alpha-containment glove box. A smaller version of the 1-kg/h unit used in the initial development activities was designed and purchased from the Mellen Company of Concord, New Hampshire. This unit produces oxide powder at a rate of approximately 100 g/h. A schematic of the rotary kiln furnace and ancillary condenser/scrubber equipment is shown in Fig. 1. This equipment was initially tested with surrogate materials and later transferred to an alpha-containment glove box for use with radioactive materials. A photo of the equipment setup in the glove box (before installation of the front glass with glove ports) is shown in Fig. 2.

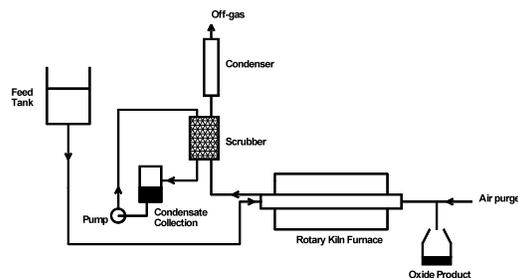


Fig. 1. Small-scale MDD schematic.



Fig. 2. Photograph of glove-box MDD unit.

EXPERIMENTAL WORK

A number of development runs with the MDD equipment described above were completed. Initial runs utilizing a cerium nitrate solution as a surrogate for actinide nitrate solutions. Testing with cerium allowed for simplified operation of the unit to establish basic parameters such as

feed flow rate, feed metal concentration, kiln operating temperature and profiles, kiln incline angle, and oxide throughputs. With the surrogate testing completed and the unit installed in the glove box, conversions of plutonium nitrate and depleted uranium nitrate, as well as co-conversion of U/Pu, U/Pu/Np, and U/Pu/Np/Am mixtures were made. These runs yielded a number of products for measuring tap density, particle size, and uniformity of the co-converted products. The need for additional physical property measurements was identified during these early tests. To generate samples for these physical property measurements, a second fume-hood-contained MDD unit was purchased and installed for making multiple small-scale runs at various operating conditions. Additional instrumentation for characterization of the MDD products was procured, including a BET surface area analyzer, a helium pycnometer for powder and pellet density, an Autotap for determining bulk and tap densities, a powder rheometer to determine flowability, a laser light scattering particle size analyzer, and an X-ray diffractometer for determining the crystalline structure of the materials. Depleted uranium oxides produced in the fume-hood MDD unit were analyzed for trial operation of the individual instruments. These additional analysis techniques will allow for better characterization of the MDD-generated products and a better understanding of the relationships between the MDD conversion process and the product properties.

The ultimate goal of the MDD development is to generate oxide products with the desired ceramic properties for pressing and sintering into fuel pellets. Several test pellets were pressed using the MDD-produced powders. The capability to sinter pellets containing transuranium actinides was limited to 1350°C, which is somewhat lower than the desired sintering temperature of 1700°C for typical fuel pellets [1, 4–6]. Some preliminary pressing and sintering tests were made, but the procurement and installation of a high-temperature sintering furnace will allow for a more comprehensive correlation of MDD powder and sintered pellet characteristics.

To perform a complete characterization of MDD powders containing transuranium element blends, the characterization equipment described above must have additional containment. To accomplish this need, the instruments are being installed in alpha-containment glove boxes to

allow for characterization of a number of desired product blends.

The Radiochemical Engineering Development Center (REDC) at ORNL has completed a series of chemical processing steps as part of the Coupled End-to-End (CETE) Demonstration on a sample of spent nuclear fuel to separate and recover a number of product fractions. Two fractions in particular – a purified uranium product and a mixed U/Pu/Np product – are ideal candidates for conversion to oxide by the MDD process. Preliminary tests were conducted with a uranium fraction, and the co-conversion of the mixed uranium/actinide product was recently completed, with the conversion of the remaining uranium product planned. Characterization of the physical properties of the product is planned, followed by pellet pressing and sintering to determine if the final pellet has the proper physical properties for fabrication and use as a recycle fuel.

RESULTS

The first run in the glove-box-contained MDD unit was with a plutonium nitrate solution, followed by two runs with uranyl nitrate solution. These runs were used to get initial basic data on the MDD equipment parameters to compare with the cerium conversions. The plutonium-only run was conducted to see if this solution could be converted to an oxide via the MDD method. The resulting oxide readily moved through the furnace to the collection vessel at the end of the kiln. The uranyl nitrate feed was used to collect uranium products for comparison with data from the early development of the MDD process. The results of the tap and bulk density measurements are given in Table I below.

TABLE I. Results of Initial MDD Runs.

Feed Solution	Bulk Density (g/cm ³)	Tap Density (g/cm ³)
Plutonium	2.2	3.0
Uranium #1	2.0	2.2
Uranium #2	0.9	1.1

The differences in the densities are attributed to a wide particle size range in the collected products and the measurement of a small-quantity sample. A bulk density of >0.625 g/cm³ is considered an acceptable powder according to standards for sinterable uranium dioxide powder [7].

Co-conversion of Mixed Actinides by MDD

Next, a series of co-conversion runs were performed to generate mixed-oxide samples [3]. The method of co-conversion gives a more consistent and uniform oxide powder than that of a blended product of individual oxides. Samples containing 90% U/10% Pu, 90.4% U/9.1% Pu/0.5% Np, and 92.3% U/7.15% Pu/0.31% Np/0.28% Am were prepared by the MDD process. All of these runs were completed without problems. Two individual samples of the U/Pu/Np/Am product were taken, and different densities were obtained. Again, it is believed that the sample size was too small or the product was not homogenous. The bulk and tap densities are given in Table II.

TABLE II. Results of Co-conversion MDD Runs.

Feed Solution	Bulk Density (g/cm ³)	Tap Density (g/cm ³)
U/Pu	2.1	2.8
U/Pu/Np	2.4	3.1
U/Pu/Np/Am	0.7	0.9
	1.1	1.6

The uniformity of the products from the runs was examined by sieving the U/Pu/Np and U/Pu/Np/Am products into three size fractions and dissolving each fraction in nitric acid and analyzing the dissolvents. In the U/Pu/Np sample, the ratios of Pu and Np were low compared with the original feed solution. One possible explanation is the presence of cerium used in the electrolytic dissolution of the original plutonium. Cerium is believed to have formed insoluble oxides with the Pu and Np fractions. An anion-exchange separation of the cerium and plutonium was performed prior to making the mixed feed for the U/Pu/Np/Am run. The dissolved product fractions from this run showed essentially all of the plutonium and neptunium dissolved in the nitric acid, and good agreement between the size fractions was obtained.

Pellet Pressing of MDD Oxides

Test pellets were pressed from the original cerium oxide MDD product. A 1.44-g sample of cerium oxide was pressed in a 0.25-in.-diameter die at ~48,600 psi using a uniaxial press. The pellet length was measured to be 0.469 in. Using a theoretical density of CeO₂ of 7.13 g/cm³, the "green" pellet was calculated to be 54% theoretical density. The pellet was then sintered

at 950°C, and the final pellet was calculated to be ~90% of theoretical.

With the procurement and installation of the fume-hood MDD unit, additional depleted uranium powder was produced by the MDD process. This powder was reduced from UO₃ to UO₂ by heating to 600°C for 4 h in a dry and a moist 4% H₂/Ar atmosphere. The moist atmosphere was obtained by passing the mixture through a gas washing bottle containing distilled water. The characteristics of the pellets are shown in Table III.

TABLE III. Pellet Properties from MDD Powders

Calcination/ Reduction	Surface Area (m ² /g)	Green Pellet (% TD)	Sintered Pellet (% TD)
1 st Group			
Dry H ₂ /Ar	3.0	49	95
Moist H ₂ /Ar	2.2	51	91
2 nd Group			
Dry H ₂ /Ar	1.8	54	92
Moist H ₂ /Ar	1.6	56	90

Some general observations can be made from these preliminary data. The second group of pellets was fabricated from powder produced at a higher rotary kiln temperature (visible U₃O₈ powder), resulting in a lower-surface-area powder. The higher-surface-area powder shows lower green pellet densities but generally higher sintered pellet densities. The moist H₂/Ar lowered the surface area of the reduced powder, leading to higher green pellet densities and lower sintered pellet densities. Additional conversions of depleted uranium solutions in the MDD unit are planned for further investigation and correlation of the various physical properties.

Conversion of CETE-Produced Products

Two main products collected in the chemical processing of ~4 kg of spent nuclear fuel are candidates for conversion by the MDD process. A purified uranium stream was collected during a co-extraction partial-partition separations operation. This stream contains ~2.9 kg of uranium in ~55 L of solution. This solution was evaporated in the hot cell evaporator to ~8 L before it was transferred to the MDD glove box. The solution was further adjusted to lower the acid concentration and prepare the MDD feed solution. This product will be converted using

the MDD process. The U/Pu/Np stream collected from the partial-partitioning separations containing approximately 165 g U, 12 g Pu, and 0.6 g Np in 7–8 L of nitric acid was transferred to the MDD glove box. After acid and chemical adjustment, this solution was converted to a mixed-oxide product using the MDD process. The MDD unit operated well, and the preliminary observation (free-flowing powder and clear condensate) indicate a good conversion of the product was obtained.

REFERENCES

1. P.A. HAAS, R.D. ARTHUR, "Development of Thermal Denitration to Prepare Uranium Oxide and Mixed Oxides for Nuclear Fuel Fabrication," ORNL-5735, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1981).
2. F.G. KITTS, "Pilot-Scale Demonstration of the Modified Direct Denitration Process to Prepare Uranium Oxide for Fuel Fabrication Evaluation," ORNL/TM-12726, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1994).
3. L.K. FELKER, R.J. VEDDER, E.A. WALKER, "Preparation of Mixed Oxides by Modified Direct Denitration," ANS Abstract, ANS Winter Meeting 2006.
4. N.C. DAVIS, C.W. GRIFFIN, "Pellet Fabrication Development Using Thermally Denitrated UO₂ Powder," PNL-4305, Pacific Northwest Laboratory, Richland, Wash. (1992).
5. O.D. SLAGLE, N.C. DAVIS, L.J. PARCHEN, "AVLIS Modified Direct Denitration: UO₃ Powder Evaluation," PNL-8481, Pacific Northwest Laboratory, Richland, Wash. (1994).
6. J.C. MAILEN, D.J. PRUETT, D.R. McTAGGART, "Direct Thermal Denitration to Prepare Mixed Oxides for Nuclear Fuel Fabrication," ORNL/TM-8197, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1982).
7. ASTM C 753-04 *Standard Specification for Nuclear Grade, Sinterable Uranium Dioxide Powder.*