

## **PLUTONIUM AND NEPTUNIUM CONVERSION USING MODIFIED DIRECT DENITRATION**

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### **Abstract**

The processing of spent nuclear fuel through the various stages of separations yields a number of product and waste streams, typically in nitric acid solutions that require conversion to a solid form for recycle, storage, or disposal. One of the product streams of interest is the separated plutonium and neptunium product, which, if successfully converted to an oxide product, could be blended with uranium oxide for recycle and further transmutation as a mixed-oxide fuel. The desire is for the conversion process to generate an oxide product with the proper ceramic properties (particle size, density, surface area) for blending and fuel fabrication without further processing steps. The modified direct denitration process was developed mainly for uranyl nitrate conversion. The purpose of this study was to investigate the use of the modified direct denitration process to convert a separated plutonium/neptunium stream to an oxide product with favorable ceramic properties for blending and mixed-oxide fuel fabrication.

### **Introduction**

The methods utilized for the processing of spent nuclear fuel continue to be investigated to determine the best options for material separations, waste minimization, further transmutation, and acceptable storage or disposal forms. A number of chemical processes for the recovery and separation of the desired product streams have been developed and are under various stages of evaluation. Early studies focused on the separation of the main actinide element constituents, i.e., uranium, plutonium and neptunium, americium and curium, into purified product streams. These streams would typically be in nitric acid and would require conversion to a solid form for recycle, storage, or disposal. One of the main product streams of interest is the separated plutonium and neptunium product, which, if successfully converted to an oxide product, could be blended with uranium dioxide for recycle and further transmutation as a mixed-oxide fuel. This oxide product would need to have proper ceramic properties (particle size, density, surface area) for blending with the uranium and fuel fabrication without further processing or conversion steps. An alternative process would involve the co-conversion of the uranium and plutonium/neptunium products to an oxide form with suitable ceramic properties for direct fuel fabrication.

The modified direct denitration (MDD) process<sup>1</sup> was developed at Oak Ridge National Laboratory (ORNL) for the conversion of uranyl nitrate solutions to a uranium oxide product. In the direct denitration of uranyl nitrate solutions, the final product is a glassy cake, which cracks into low-surface-area pieces. This material would require extensive grinding, ball-milling, calcining, or other such methods to improve the ceramic properties for fuel fabrication. It was determined that an additive to the uranyl nitrate solution can change the final product to fine powder with ceramic properties suitable for pellet fabrication. The oxide produced by this method shows comparable ceramic properties to that produced by the more traditional ammonium diuranate (ADU) precipitation conversion process used for power reactor fuels fabrication.

The purpose of this study was to (1) establish the capability to prepare oxides by the MDD method on a laboratory scale, (2) convert plutonium/neptunium product fractions from a nitrate solution to an oxide product by the MDD method and compare the ceramic properties with those of an oxide produced by precipitation/calcinations methods, and (3) evaluate the co-conversion of uranium and plutonium/neptunium nitrate solutions for direct fuel fabrication. Presently, equipment for producing oxide products by the MDD method has been designed, tested, and installed in an alpha-containment glove box. Preliminary tests with pure plutonium feeds have been conducted with favorable results.

## **Equipment**

Various types of processing equipment for denitration processes have been evaluated,<sup>2</sup> and some have been used for larger-scale production with low-enrichment uranium feeds. Conversions of spent fuel containing uranium and plutonium would require criticality control and remote operation, which greatly influence the choice of equipment. The continuous rotary kiln with breaker bars appears to be the most promising choice for this type of operation. Larger-scale commercial units (kgs/h) are available, but a smaller test unit (grams/h) was desired for this work. A laboratory-scale unit was designed and purchased from The Mellen Company of Concord, New Hampshire. A schematic of the rotary kiln furnace and ancillary equipment is shown in Figure 1.

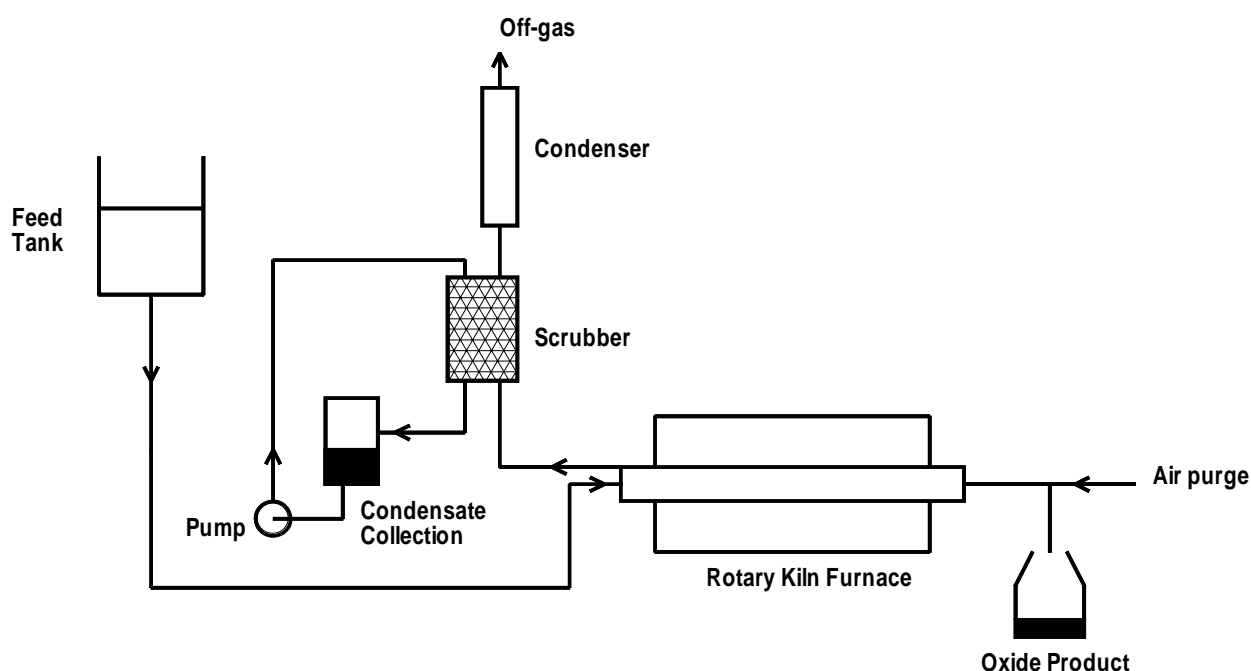


Figure 1. Schematic of process equipment

An MDD run begins with the heat-up of the furnace concurrent with rotation of the heated pipe. The ancillary systems—vacuum, cooling water, off-gas scrubber, etc.—are started. These also include the air purge, which enters the kiln from the product side and serves to keep off-gas away from the product. When the furnace has reached steady-state operating temperature, water addition is started. The purpose is to cool the feed tube sufficiently to prevent feed from decomposing inside the line and plugging it. After a short while, feed addition begins, and then the operating conditions (e.g., feed rate, vacuum, temperatures) are monitored. The product is collected in bottles, which are exchanged as they fill.

## Experimental

The initial testing of the MDD process involved the establishment of operating parameters for the new equipment. This work was performed with the unit in a laboratory hood, using cerium nitrate solutions as a surrogate for a plutonium feed. A number of basic parameters were determined, such as furnace temperature, feed rates, incline angle, tube rotation rate, air purge rates, and vacuum settings with the test equipment. These tests were followed by studies with the cerium nitrate surrogate to determine feed concentration and addition rate, chemical ratios, material balances, condensate carryover, and condensate recycle.

### ***Cerium nitrate testing***

The most significant operating variables are furnace temperature, angle of incline, tube rotation speed, air purge rate, and feed composition and addition rate. The impact of the variables was studied initially in short-duration scoping tests and then subsequently in longer-duration runs in which steady state was reached. Steady state is considered to be reached when the powder accumulation rate and consistency are uniform, the internal temperatures are stable, and the fumes in the condensate pot are of consistent intensity. At a given feed rate, the angle of incline and the heated tube rotation speed determine the residence time inside the kiln. Data from the tests showed a linear relationship between the conveyance rate and angle of incline, with the slope depending upon the tube rotation speed. A slight incline of the rotary kiln produces smoother operation with less temperature fluctuations, uniform off-gas intensity, and constant product accumulation. Finer adjustment of residence time can be achieved by varying the tube rotation speed. Feed composition has a significant impact. The feed should be as concentrated as possible, within the solubility limits, to minimize the evaporative load on the furnace. The air purge enters the kiln from the product end, counter-current to the product flow, helping to move vapors out of the kiln and keep them away from the product. The flow must be sufficient to do this without entraining powder in the off-gas.

The material balances—calculated from the feed and product (assumed to be cerium oxide)—less volatiles, indicate that only a small amount of the product is lost to the off-gas. There is, however, a fine layer of oxide that coats the inside of the kiln, complicating the material balance. Additionally, condensate from a run was filtered and found to contain little of the solids (the cerium oxide would not be highly soluble). After denitration operations, the volume of condensate was measured and condensate samples were titrated to determine the nitric acid content. Direct analysis of the off-gas was not performed.

Observation of the powder exiting the furnace revealed that the particles are small but agglomerated or molded into larger clumps. These larger clumps of powder were easily broken down into small particles. A sieving operation was used to characterize the particle sizes, which easily fractured the clumps into smaller particles. The sieving was not a prolonged operation, but rather a short test to determine the particle size and the durability of the agglomerated particles. The tap densities of the cerium oxide powders were measured by pouring the powder into a graduated cylinder, tapping gently at the mid-wall of the cylinder, and measuring the weight and volume. Processing the oxide through a series of sieves increased the density of the product.

Because the MDD operation results in some loss of material to the condensate, techniques for recycling this condensate back to the feed were investigated. The condensate was neutralized to a basic solution and the precipitate settled producing a clear supernate. The supernate was decanted for disposal, and the remaining slurry was recycled back to the feed solution. Thus, the recycle technique results in minimum waste generation.

### ***Plutonium nitrate testing***

After the initial testing with cerium nitrate surrogate solutions was completed, the equipment was transferred to an alpha-containment glove box for operation with radioactive constituents. The first test with plutonium nitrate solutions has been completed. The run conditions were approximately those developed in the cerium tests. The feed solution contained a lower than desired plutonium concentration and a higher acid concentration. These conditions will be corrected in future tests. There was a somewhat greater off-gas to product ratio in this run than typical or desirable which may cause higher entrainment. The loss to the condensate was higher than was experienced with the cerium testing. This was initially attributed to making a finer powder that was more easily entrained.

However, examination of the product produced showed it to be relatively dense. A final tap density in the range of 2.5 to 3.5 g/mL was obtained. The powder flowed freely and did not tend to stick to the walls of the graduate.

Analyses of samples of the condensate showed a total of 0.3 g of plutonium in solution with an acid concentration of 5.5 N. However, the entrained oxide does not appear to be very soluble in the condensate and is therefore not included in this inventory. The  $\text{NH}_4\text{OH}$  precipitation technique developed in the cerium testing was applied to the condensate to recover plutonium. The total amount of plutonium in the resulting supernate was  $1.0 \times 10^{-3}$  g. There was initially 0.3 g in solution, so the precipitation reduced the plutonium in solution by a factor of  $\sim 300$ .

## Conclusions

Equipment and techniques for conversion of metal nitrate solutions to metal oxides by the MDD process have been established and tested. Further development and installation of the equipment in an alpha containment glove box will allow conversion of actinide solutions to actinide oxide products. The current work is focusing on pure plutonium solutions; future plans are to convert plutonium/neptunium mixtures and incorporate co-conversion of uranium/plutonium solutions with the addition of neptunium or other minor actinides. The ceramic properties of these products will be compared with those of products produced by the more traditional precipitation/calcination methods. If favourable ceramic properties can be produced, this method of conversion could be incorporated into the spent fuel processing schemes to yield products ready for recycle and further transmutation.

## REFERENCES

- [1] R. E. Lerch and R. E. Norman, "Nuclear Fuel Conversion and Fabrication Chemistry," *Radiochimica Acta*, 36, pp 75–88 (1984).
- [2] R. J. Sloat, *et al.*, *Processing Alternatives for Uranium-Plutonium Conversion*, NEDG-21951, General Electric Co., San Jose, California, 1978.