

Equipment and Method Choices for Concentration and Denitration of the Uranium Product from UREX

Chemical Science and Engineering Division

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by

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EQUIPMENT AND METHOD CHOICES FOR CONCENTRATION AND DENITRATION OF THE URANIUM PRODUCT FROM UREX

ABSTRACT

A review of previous work at Argonne National Laboratory (Argonne) and the literature was conducted on potential means of converting the uranium (U) product from the uranium extraction (UREX) process to uranium oxide (UO₃) powder. In this context, UREX is a means of purifying the irradiated SHINE target solution. Two general methods are discussed: (1) direct denitration, which has the advantages of simplicity and technical maturity and the disadvantage of a final product that is not optimized for dissolution; and (2) modified direct denitration (developed at Oak Ridge National Laboratory), which has the advantage of generating an excellent product and the disadvantage of lower technical maturity. Modified direct denitration should be carried out in a simple pot calciner to treat the small (approximately 3 L) amount of uranium product to be generated in mini-contactor-scale studies at Argonne.

1 INTRODUCTION

Several methods have been described for converting dilute nitrate solutions to uranium oxide product (Shaw et al. 1961; Vandegrift 2000). The process for this particular application requires an adequate throughput, minimal uranium loss, and high purity of the UO_3 product. Several chemical denitration methods have been described that produce UO_2 solid product (Bakel et al. 2003). Because UO_3 is the required product in this project, options for the production of UO_2 will not be discussed here.

2 DIRECT DENITRATION

The first method described here for the treatment of dilute uranyl nitrate/nitric acid solutions is simple direct thermal denitration. Direct denitration is best described as a two-step process: (1) evaporation and (2) decomposition. The first step is the evaporation of water and nitric acid from the solution producing a uranium nitrate hexahydrate molten salt. During the second step, the molten salt loses its waters of hydration and nitrate simultaneously to produce solid UO_3 . The evaporation step is easily carried out and controlled by maintaining the nitrate solution at its boiling point; the condensate can then be collected for potential recycle. The somewhat violent decomposition step is difficult to control and can involve a great deal of foaming and splattering. The melting point of the uranyl hexahydrate salt is significantly lower than the decomposition temperature, so a syrupy molten salt is formed during heating (Collins 2013). When this molten salt reaches its decomposition temperature, water vapor and NO_x gases escape. This leads to splattering and foaming (Kitts 1994; Felker et al. 2008), and the uranium can be spread throughout the treatment apparatus.

Some advantages of direct denitration are that the process is simple and that it can be performed in a variety of apparatuses (Collins 2013). In addition, it is a well-understood process that has been deployed at large scales using a wide variety of equipment (Sloat 1978). Disadvantages are that the uranium can be spread throughout the treatment apparatus and that the product is massive, rather than a free-flowing powder (Bakel et al. 2003). The massive nature of the final UO_3 product has been shown to be a particular issue if a pot calciner is used in batch mode. Under such conditions, the product is difficult to recover, so recovery might be incomplete. In addition, the product is typically agglomerated and composed of large grains that provide a relatively low surface area, which could slow the rate of subsequent dissolution (Collins 2013). Several approaches utilizing particular processes or equipment have been developed that are reported to improve the properties of the final product.

Precise control while heating the molten salt can improve the properties of the final UO_3 product by ensuring that the dehydration is largely complete before denitration begins. This effectively avoids the formation of the molten salt, thus avoiding splattering and the formation of a massive product. Hobbs and Parkes (2004) provide an example of this approach. In their approach, which was developed for preparing mixed Pu/U oxides for mixed oxide (MOX) fuel, the first step is to dry the mixed uranyl-plutonyl-nitrate solution in a vacuum oven at 50°C to produce a solid, mixed dihydrate nitrate salt that decomposes before it melts. The salt was then calcined at 550°C in a rotary furnace with a breaker bar (a steel rod that rolls freely inside the rotary furnace to prevent solids from building up on the furnace wall) to produce a solid MOX powder product. The rotary furnace effectively forms a thin film of dihydrate salt and UO_3 product. The MOX powder resulting from this method was free flowing and had a high surface area appropriate for efficient dissolution.

A microwave-heating batch process accomplishes denitration of uranium nitrate solutions using controlled, uniform heating to complete the dehydration step prior to the commencement of the denitration step (Notz and Haas 1981; JAEA 2009). In this way, the formation of the molten salt and the resulting undesirable massive nature of the product can be avoided.

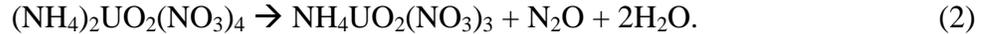
Direct denitration is a well-understood and versatile method that has been used with a wide variety of feeds and, lot sizes, and equipment. The property of the final UO_3 product can be greatly improved by slow, controlled heating.

3 MODIFIED DIRECT DENITRATION

Modified direct denitration is a well-studied process developed at Oak Ridge National Laboratory (Notz and Haas 1981; Kitts 1994; Felker et al. 2008). It is best described as a five-step process: (1) double-salt formation, (2) evaporation of the water and nitric acid, (3) dehydration of the double salt, (4) partial denitration, and (5) full denitration/oxide formation (Figure 1). Ammonium nitrate is typically added to the uranyl nitrate feed prior to heating (Kitts 1994). The second step is the evaporation of the water and nitric acid (Felker et al. 2008). The third step is to dehydrate the double salt at about 40°C to form an anhydrous double salt:



In the fourth step, the anhydrous salt loses one mole of ammonium nitrate without melting at about 170°C:



Finally, amorphous UO_3 forms after complete denitration at about 270°C:



Further heating to 500°C results in a crystalline UO_3 product (Notz and Haas 1981).

Some advantages of modified direct denitration are that it is easily controlled and produces a free-flowing high-surface-area UO_3 powder, and it is based on well-understood chemical processes. A rotary furnace has been used to perform the denitration steps (Felker et al. 2008). Operation of the furnace is quite simple and straightforward; the furnace temperature is held at a constant value. The furnace is held at a fixed inclination and is rotated at a constant speed while the liquid feed is metered in at a constant rate (Kitts 1994). The UO_3 product is a free-flowing powder, so is easily handled. In addition, the powder has a high surface area and is, therefore, ideal for subsequent dissolution and recycle (Collins 2013). Disadvantages are that it is a complex, multistep process that might not be amenable to high throughput and that has not been deployed in a large industrial scale. However, if (1) the batch sizes are relatively small (i.e., kilogram scale), and (2) high throughput is not required, this process could be optimized for the desired application.

The details of the process developed at Oak Ridge National Laboratory provide a good starting point. An aqueous feed containing uranyl nitrate and ammonium nitrate at NH_4^+/U ratios of about 2.6 is introduced into the heated portion off a 4-in.-internal-diameter stainless steel pipe rotating within a rectangular furnace maintained at about 600°C (Kitts 1994). The liquid is evaporated immediately, leaving a solid double nitrate salt that decomposes to a fine powder without melting or going through a gummy, molten stage. This approach combines steps 2 through 5 as well as the crystallization step. As stated, this is in fact a continuous process. The cited work used a feed rate of about 25 mL/minute of a relatively concentrated uranyl-ammonium nitrate solution (500 g U/L, with a NH_4^+/U molar ratio of about 2.6) (Kitts 1994).

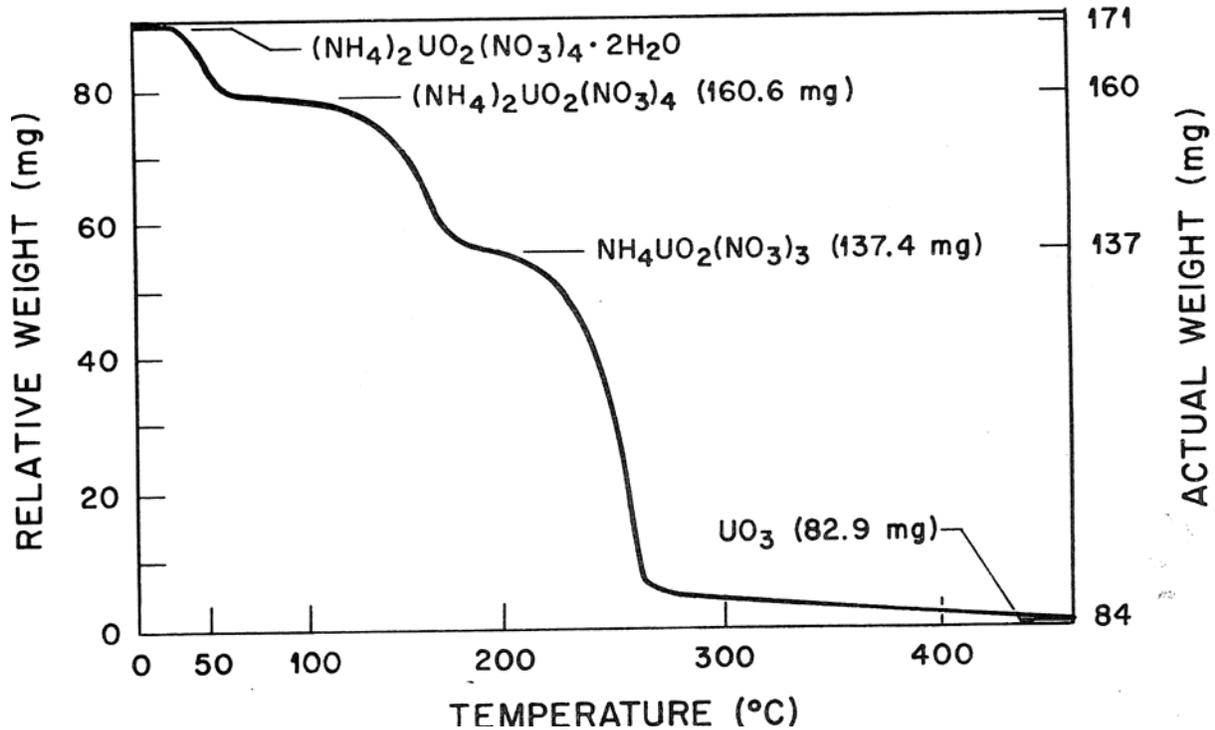


FIGURE 1 Thermogravimetric Analysis of the Uranyl-ammonium Nitrate Double Salt (initial sample weight was 171 mg; Notz and Haas 1981)

Two 1-inch-diameter stainless steel breaker bars rotate on the inside surface of the heated section of the furnace to assist with the heat transfer and to prevent the buildup of a thick layer of solid at the point of evaporation. The product exits the lower end of the furnace, countercurrent to an air purge, as a free-flowing powder (Kitts 1994).

The modified direct denitration method is well studied at the laboratory scale and might be adapted for the scale needed in this project. The utilization of a rotary furnace is reported to simplify utilization of the process.

4 SMALL-SCALE TREATMENT OF UREX SOLUTIONS AT ARGONNE

A small-scale denitration of UREX product solution will be done to generate a free-flowing, high-surface-area powder UO_3 product. While Morgridge Institute of Research is considering a fluidized-bed direct-denitration approach, the tests at Argonne National Laboratory will be at a scale that is not amenable to this technology. This report has described and reviewed several alternative approaches that would be appropriate for the approximately 3 L of UREX product solution expected from the two 2-cm centrifugal contactor demonstrations to be performed in the 2013 Fiscal Year (FY-13).¹ Several properties of the solid product will be required of both the Argonne work and the larger-scale process as deployed: (1) high surface area (i.e., fine grained); (2) low UO_2 and U_3O_8 content; and (3) free flowing. The first two properties will assist in rapid and complete dissolution in sulfuric acid and the third property will lead to easy product handling.

The second and third rounds of SHINE-solution cleanup FY-13 research and development at Argonne will test the sulfate-to-nitrate conversion, as well as removal of fission and activation products from the uranyl-nitrate product solution. A full UREX-process demonstration will be conducted using a 33-stage 2-cm centrifugal contactor located in a glovebox. After the UREX process, technetium (Tc) and iodine (I) will be removed from the uranium product solution using an anion-exchange column. The resulting pure uranyl-nitrate solution will be concentrated and then denitrated to produce UO_3 . The UO_3 will then be dissolved in sulfuric acid to reconstitute the SHINE target solution composition. The denitration process carried out at Argonne will be designed specifically to generate a solid UO_3 product amenable to dissolution.

¹ The first will use a depleted-uranium solution spiked with a solution of a depleted uranium (DU) foil irradiated at the linac. The second will use between 0.5 and 1 L of irradiated mini-SHINE target solution that has been converted from sulfate to nitrate media.

5 RECOMMENDATIONS

Two laboratory approaches are proposed here: (1) direct denitration in a pot calciner followed by crushing and (2) modified direct denitration in a pot calciner. Details of the first approach have been previously reported (Bakel et al. 2003). The solution to be treated will be approximately 3 L of UREX product. Several properties of the solid product will be important: (1) high surface area (i.e., fine grained), (2) low UO_2 and U_3O_8 content, and (3) free flowing. The first two properties will assist in rapid and complete dissolution in sulfuric acid, and the third property will lead to easy product handling.

For the first approach, a laboratory-scale calciner has been fabricated that consists of a 250-mL calcination pot (Figure 2) heated using a standard box furnace (Figure 3). The concentrated uranyl-nitrate solution (~500g U/L) will be fed into the heated pot in order to evaporate the water and nitric acid, which will be recovered using a simple water-cooled condenser. The operating conditions for similar system have previously been evaluated and optimized at Argonne (Bakel et al. 2003).

After evaporation, the furnace temperature will be increased to the decomposition temperature. It is observed that the melting temperature of the salt is lower than the decomposition temperature so that a molten salt pool forms at the bottom of the pot. The denitration reaction occurs and mixed NO_x gasses are released. These can be recovered by scrubbing the off-gas through a basic solution. This simple method will produce a solid massive product that will need to be mechanically removed from the pot and crushed in order to be readily dissolved in sulfuric acid.

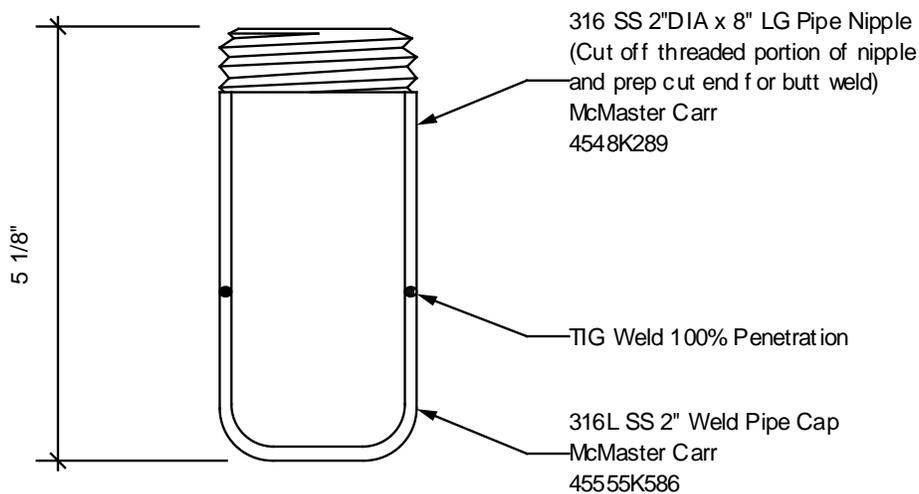


FIGURE 2 Detailed Drawing of the Calciner Pot

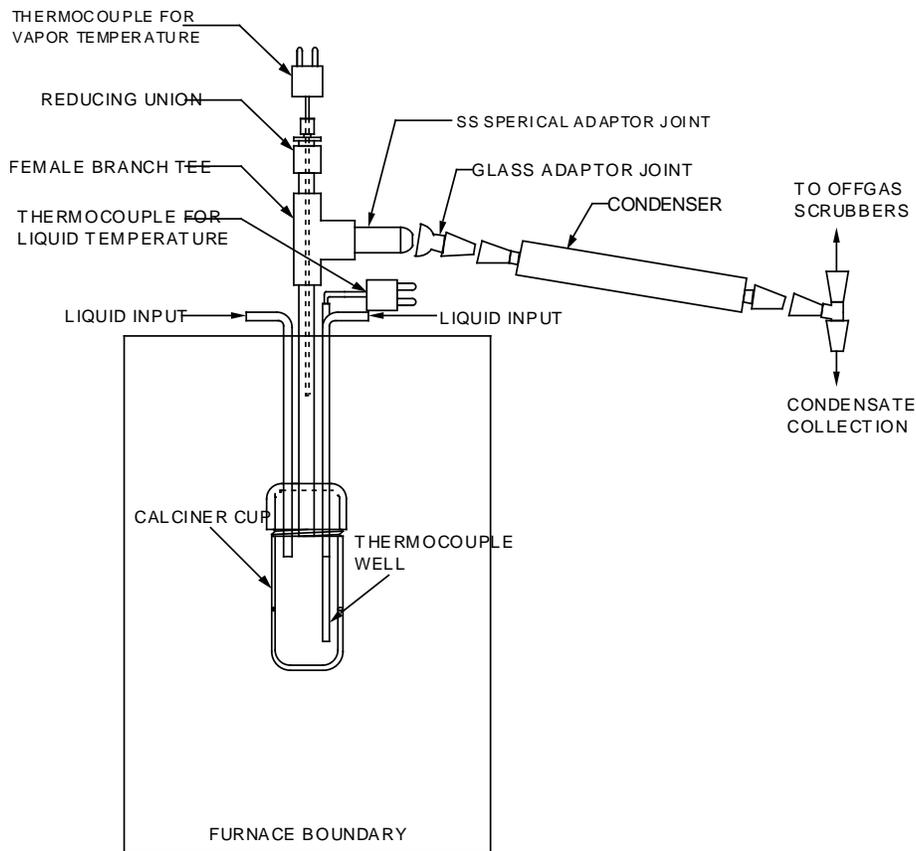


FIGURE 3 Schematic Diagram of Previously Used Calciner Equipment Suggested for Use in This Project

The second approach would use the same apparatus shown in Figure 2. In this case, solid ammonium nitrate would be added to the concentrated-uranium-nitrate feed solution prior to treatment. The ammonium-uranyl nitrate solution will be fed into the heated pot to evaporate the water and nitric acid. These will be recovered using a water cooled condenser. After evaporation, the furnace temperature will be increased to the decomposition temperature (Figure 1). As the temperature in the calciner pot increases, the hydrated ammonium-uranyl nitrate salt decomposes (dehydration followed by denitration with no melting of the double salt). The product will be an amorphous UO_3 powder that crystallizes at about 500°C . This method is expected to produce a high-surface-area, free-flowing UO_3 powder that is ideal for dissolution in sulfuric acid.

Based on the information reviewed here, proceeding with a small-scale test of the modified direct denitration process is recommended. Direct denitration should be reserved as a backup if the modified direct denitration is later determined to be not applicable.

6 REFERENCES

Bakel, A.J., K.J. Quigley, and G.F. Vandegrift, 2003, *Argonne National Laboratory Progress in Minimizing Effects of LEU Conversion on Calcination of Fission Product ⁹⁹Mo Acid Waste Solution*, Reduced Enrichment for Research and Test Reactors 2002 International Meeting, San Carlos de Bariloche, Argentina.

Collins, E.D., 2013, personal communication from Collins (Oak Ridge National Laboratory) to A. Bakel (Argonne National Laboratory), February 16.

Felker, L.K., R.J. Vedder, E.A. Walker, and E.D. Collins, 2008, *Product Conversion: The Link between Separations and Fuel Fabrication*, ATALANTE 2008.

Hobbs, J.W., and P. Parkes, 2004, *Production of MOX Pellets from Plutonia and Mixed Oxide Powders Prepared by Direct Thermal Denitration*, ATALANTE 2004.

Japan Atomic Energy Agency (JAEA), 2009, *Summary of Microwave Heating Denitration Process*, FCT-FF-JP-002-1, Fuel Cycle Technology Working Group.

Kitts, F.G., 1994, *Pilot Scale Demonstration of the Modified Direct Denitration Process to Prepare Uranium Oxide for Fuel Fabrication Evaluation*, ORNL/TM-12726, Oak Ridge National Laboratory.

Notz, K.J., and P.A. Haas, 1981, *Properties and Thermal Decomposition of the Double Salts of Uranyl Nitrate-Ammonium Nitrate*, ORNL/TM-7820, Oak Ridge National Laboratory.

Shaw, W.E., W.C. Manser, R.G. Geier, and S.H. Smiley, 1961, "Natural, Slightly Enriched, or Depleted Uranium Chemistry," p. 345 in: *Reactor Handbook*, 2nd ed., Vol. II, Fuel Reprocessing, M. Stroller and R.B. Richards (editors), Interscience Publishers, New York.

R.J. Sloat, 1978, *Processing Alternatives for Uranium-Plutonium Conversion*, NEDG-21951, General Electric Co.

Vandegrift, G.F., 2000, *Transformation of UREX Effluents to Solid Oxides by Concentration, Denitration, and Calcination*, ANL-00/25, Chemical Technology Division.



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