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Direct Thermal Denitration to Prepare Mixed Oxides for Nuclear Fuel Fabrication

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D. J. Pruett
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CONSOLIDATED FUEL REPROCESSING PROGRAM
C F R P ORNL

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Consolidated Fuel Reprocessing Program

DIRECT THERMAL DENITRATION TO PREPARE MIXED OXIDES FOR NUCLEAR FUEL FABRICATION

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Chemical Technology Division

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DIRECT THERMAL DENITRATION TO PREPARE MIXED OXIDES FOR NUCLEAR FUEL FABRICATION

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ABSTRACT

Direct thermal denitration of nitrate solutions containing uranium, plutonium, and about 2 mol of ammonium nitrate per mol of heavy metals produced a mixed oxide powder which was well suited to the production of pellets. The nitric acid concentration of the solutions was maintained at greater than 1 M to prevent hydrolysis of the plutonium. The resulting UO_3-PuO_2 powder had a bulk density of about 1.2 g/cm^3 and required preslugging before pellet pressing. Pellets prepared at the Oak Ridge National Laboratory (ORNL) by pressing at 241 MPa (35,000 psi) or 310 MPa (45,000 psi) and sintering at 1450°C for 4 h had densities of 95% of theoretical, good external appearances, and good microstructures. The pellets were completely soluble in refluxing 7 M HNO_3. Pellets were also pressed from this powder at Battelle Pacific Northwest Laboratory (PNL) with similar results.

A sinterable PuO_2 product was obtained in comparable denitration tests with plutonium solutions, although the powder had poor flowability and produced pellets with scattered, relatively large porosities. The results, however, encourage further development of better plutonia powder by this process.

1. INTRODUCTION

Current regulations for reprocessing nuclear fuel require that the plutonium product be shipped in an insoluble form, most likely as the oxide. Thus, the conversion of uranium and/or plutonium nitrate solutions from Purex separations into oxide forms is a primary part of reprocessing; this oxide product should be suitable as a feed material

for pellet fabrication. Recent proposals to coprocess plutonium with uranium call for a process to convert solutions containing both uranium and plutonium directly into mixed oxides. Direct thermal denitration of the product stream from the Purex plant is one possible product conversion method. The several potential advantages of this approach include:

1. a minimum of process steps,
2. plutonium is not necessarily separated as a pure stream, and
3. the waste streams are few in number and generally compatible with the Purex plant.

A number of earlier studies examined the thermal denitration of uranium nitrate or plutonium nitrate as separate feeds; these studies are referenced and summarized by Haas et al.[1] The direct thermal denitration of plutonium nitrate solutions in a screw calciner had been found to give an acceptable powder which was blended with UO_2 to produce good quality pellets.[2] However, direct thermal denitration of uranyl nitrate solutions had generally given a poor product primarily due to the "mastic" stage which appears during evaporation of the water and nitric acid. A major breakthrough in this area occurred when Haas et al.[1] discovered that by introducing ammonium nitrate into the uranyl solution, the solution could be denitrated without formation of a mastic stage. The mastic stage is eliminated by the formation of double salts between the uranyl nitrate and ammonium nitrate.[3] This behavior has been confirmed with additional data obtained in TGA/DTA studies.[1] The double salt first dehydrates to the anhydrous double salt which subsequently decomposes to yield a finely powdered UO_3. The ammonium nitrate decomposes largely to yield N_2O, N_2, O_2, and H_2O (NO_x is formed from decomposition of the metal nitrates). Haas constructed a rotary kiln and used it to demonstrate the production of UO_3 powder by direct denitration of uranium solutions containing ammonium nitrate. Good quality pellets were produced from this powder at both ORNL and at PNL. Larger-scale denitration runs were made using a rotary kiln at the National Lead of Ohio facility at Fernald, Ohio. Powder from these tests was also found to produce good-quality pellets.

Two facts suggested that good-quality mixed oxide powders could be produced by the ammonium nitrate addition technique: (1) the addition of ammonium nitrate to uranium solutions promoted the production of good-quality UO_2, and (2) good-quality PuO_2 powder was successfully produced by direct denitration in the absence of ammonium nitrate. A scouting task was therefore initiated to prepare a simulated coprocessing product solution, use it in a continuous conversion process, test the products by fabrication of pellets in a standard sinterability test, test the homogeneity of the pellets by a dissolution test, and supply samples for fabrication tests. This report details these scouting studies.

2. EXPERIMENTAL

2.1 Preparation of Plutonium Solution

Plutonium for these studies was obtained in the form of plutonium oxide of the following isotopic composition:

^{242}Pu	0.2 at. % of Pu
^{241}Pu	1.2 at. % of Pu
^{240}Pu	11.5 at. % of Pu
^{239}Pu	87.0 at. % of Pu
^{238}Pu	0.05 at. % of Pu
^{241}Am	0.54 at. % of total heavy metals

The gamma radioactivity of this material made it desirable to remove the americium in the course of preparing the plutonium nitrate stock solution. Gamma radiation measurements at the face of the glove box were 10 mR/h for 50 g of the solid and 20 mR/h for its solution before processing.

Fifty grams of the oxide was dissolved, using a standard plutonium procedure, in about 300 mL of 8.0 M HNO_3–0.02 M HF solution (initial composition) in a glass system consisting of a round-bottom distillation flask and a condenser cooled with chilled water. Concentrated hydrofluoric acid was added at about 5-h intervals in a quantity sufficient to increase the HF concentration by about 0.02 M. Periodic addition of HF is necessary to replace that lost by reaction with the silica of the

glass system and by reaction with dissolved plutonium to form stable plutonium fluoride complexes. At the end of about 15 h (two additions of HF), the oxide was essentially dissolved. The refluxing was continued for an additional 3 h to remove the remaining HF from the solution; HF reacts with the silica of the flask to form volatile silicon fluoride which escapes from the solution. Additional decontamination from fluoride probably occurs during a subsequent peroxide precipitation step. The acid solution was cooled and filtered through a Teflon filter medium to remove undissolved residue.

The plutonium was recovered as the peroxide by adding an equal volume of about 30 wt % hydrogen peroxide solution containing 0.5 M HNO_3 to make the solution about 4.4 M in hydrogen peroxide (estimate assumes complete plutonium precipitation) and aging the reaction mixtures overnight to achieve equilibrium. The precipitate was separated by filtration, washed with 2% hydrogen peroxide containing 0.3 M HNO_3, and air-dried. The plutonium stock solution was obtained by dissolving the solids in 300 mL of 5 M HNO_3, stirring vigorously for 6 h at room temperature, and digesting overnight without stirring. In a later preparation, allowing the precipitate to stand quiescently in the HNO_3 was found to be sufficient. The initial concentration of the acid was chosen to give about 2 M HNO_3 in the solution after decomposition of the plutonium peroxide. Other acid concentrations should be equally effective. The volume of the acid was selected to provide a stock solution containing about 150 to 200 g of plutonium per liter. The decomposition of the plutonium peroxide proceeded smoothly and without difficulty. Finally, the solution was refluxed for several hours to ensure complete decomposition of any residual hydrogen peroxide.

The reaction of plutonium with hydrogen peroxide,

$$2Pu^{4+} + 3H_2O_2 + H_2O \rightleftharpoons Pu_2O_7 \downarrow + 8H^+ , \qquad (1)$$

is probably similar to that of thorium.[4] The equilibrium solubility constant of plutonium in acidic hydrogen peroxide solution at 15°C is given by;[4]

$$K = \frac{[Pu^{4+}][H_2O_2]^{3/2}}{[H^+]^4} = 2.1 \times 10^{-5} \ . \qquad (2)$$

It was assumed that the equilibrium solubility constant at room temperature (about 22°C) would be similar. If the final acid concentration in the dissolver solution is 5 M and if the plutonium is assumed to be quantitatively precipitated by the addition of an equal volume of about 30 wt % hydrogen peroxide solution, the final acid concentration would be about 3.7 M. According to Eq. (2) the plutonium left in solution would be 0.00043 M, 0.14% of the initial plutonium.

Americium, the major gamma emitter in the stock plutonium oxide, did not form an insoluble peroxide under the highly acidic conditions used here; consequently, the americium content of the final waste solution from the precipitation was found to account for 99.3% of the gross alpha activity. Thus, the single precipitation isolated the bulk of the americium in one waste solution. About 99.6% of the americium was separated from the plutonium, and the gamma activity of the plutonium solution was reduced by a factor of about 20.

The procedure described here for preparing a plutonium stock solution produces a single, highly concentrated solution of any desired acidity with a minimum of equipment and glove-box space and with excellent americium decontamination.

2.2 Equipment

A small rotary calciner, modeled after the larger unit developed by Haas,[1] was designed and constructed. The unit (Fig. 1) consisted of a 2.54-cm (1-in.)-diam titanium tube rotated at 10 rpm within a 2.54-cm (1-in.)-diam (nominal), 15.24-cm (6-in)-long furnace containing a nickel liner to spread the high-temperature zone. The furnace was operated at about 550°C; the temperature within the center portion of the tube was about 450°C. A slope of about 2 degrees caused the powder to be transported slowly through the tube to the exit. The residence time of the powder in the tube was about 7 min. A stationary titanium scraper bar continuously removed any deposited powder from the tube wall. A FMI

pump (Fluid Metering Inc., Oyster Bay, NY), which was added as a replacement for the syringe pump after the photograph (Fig. 1) was made, fed solution directly into the titanium tube at about 1 mL/min. This modification to the system was also made after the photograph (Fig. 1) was taken; in the earlier version the feed entered the top of the packed column. A vacuum system drew air in through the exit of the calciner tube, countercurrent to the powder flow, to prevent nitrogen oxides from exhausting into the glove box. The gas-laden air left the calciner through an air-cooled packed column; nitric acid condensed from the air stream served as a scrubbing liquid for any powder blown out of the calciner by the countercurrent air stream. After passing through the packed column, the gas-air stream entered a water-cooled condenser to remove the bulk of the water and acid. Finally, the gas stream was scrubbed with water before being exhausted to the glove box.

2.3 Conditions Used for Pellet Fabrication

Pellets were produced using a standard procedure which was developed for fabrication of pellets and assessment of the sinterability of thermally denitrated UO_3 powder.

The powder was worked through a 20-mesh sieve, calcined at 600°C for 4 h in an 4% H_2-Ar atmosphere, and cooled to room temperature in CO_2. Pellets were pressed from the calcined powder at either 241 MPa (35,000 psi) or 310 MPa (45,000 psi) and sintered at 1450°C for 4 h after a heatup schedule of 300°C/h to 900°C and 100°C/h from 900 to 1450°C all in 4% H_2-Ar. The pellets were cooled in argon. Sintered densities were determined from the pellet geometry and expressed as percent of theoretical density (% TD).

Mixed oxide powder also was sent to Battelle Pacific Northwest Laboratory to be fabricated into pellets. The powder was calcined at 600°C in 4% H_2-Ar for 4 h and pressed into pellets which were sintered at 1700°C for 4 h subsequent to heating at 150°C/h to 450°C and then 300°C/h to 1700°C. The pellets were cooled to room temperature at 300°C/h. This sintering cycle was conducted in 4% H_2-Ar.[5]

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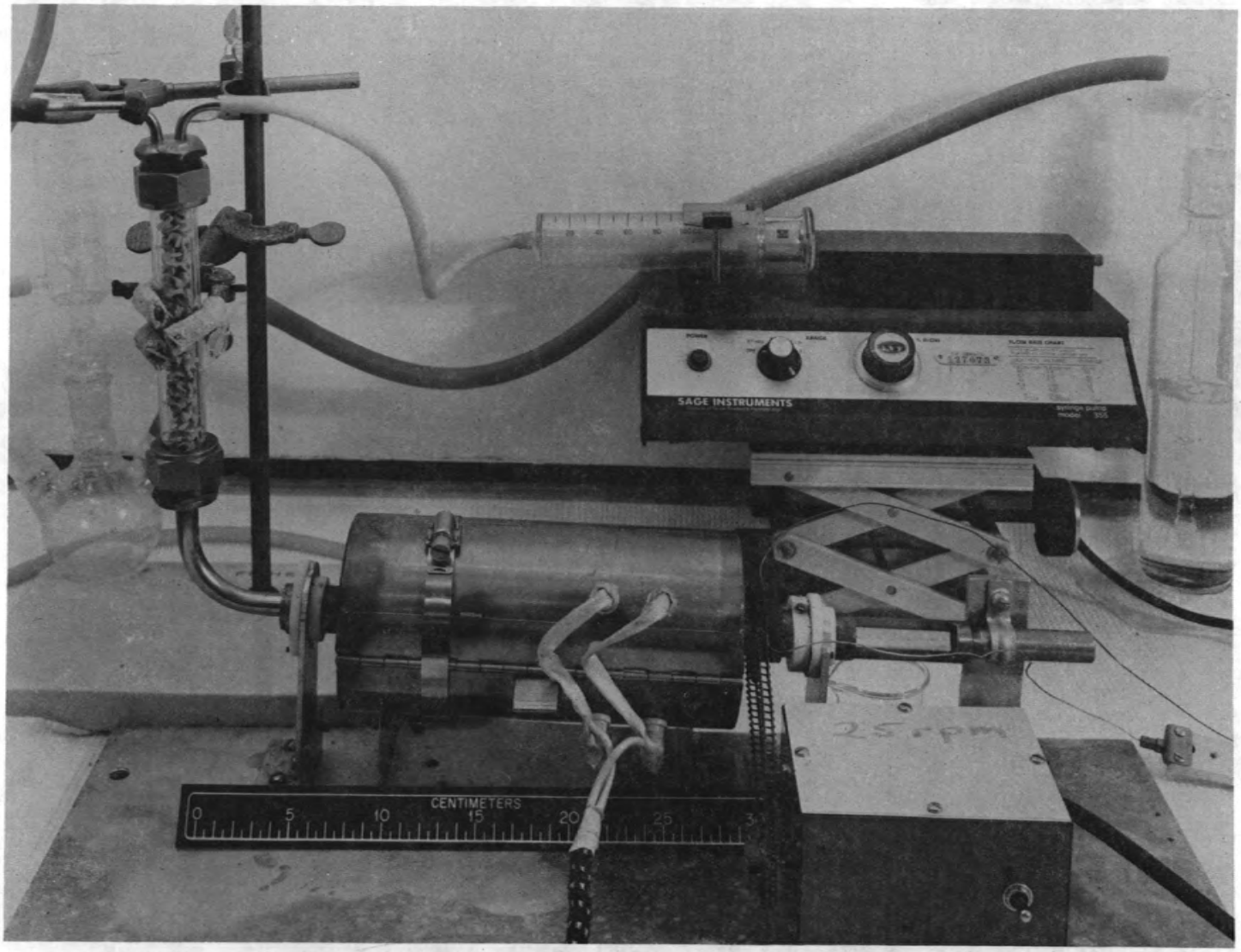

Fig. 1. Miniature rotary calciner and off-gas system.

2.4 Uranium–Plutonium Studies

Two batches of mixed uranium–plutonium oxide powder (22% Pu) were made using two different sources of uranyl nitrate to prepare feeds containing about 250 g of heavy metals per liter. The first batch of powder produced pellets of undesirable porosity (Fig. 2). The reason for this could not be determined, but subsequent investigation indicated that the first uranyl nitrate stock solution contained about 1 wt % cerium and 3.5 wt % sodium impurities. These particular impurities probably would not cause the observed porosity, but the presence of other undetected impurities was suspected. A better uranium feed was used to produce a second batch of thermally denitrated powder with a plutonium content of about 22.4% of the heavy metals and a bulk density of about 1.2 g/cm^3. The pellet which was pressed from this powder at 241 MPa (35,000 psi) is shown in Fig. 3; a pellet pressed at 310 MPa (45,000 psi) had a similar appearance. Both sintered pellets had densities of 95% TD, and were free of the porosity observed in pellets produced from the first batch of powder. Additional sintered pellets, pressed from this batch of powder, were used in dissolution tests. The pellets were completely dissolved by refluxing for 19 h in a HNO_3 solution (initial concentration 7 M); complete dissolution was estimated to have occurred in about 15 h. A plot of fraction remaining vs time (Fig. 4) was nearly linear. The plutonium contents of the solutions of the first half and the last half of a pellet were 22.3% and 22.4% of the heavy metals. The last half and the last 20% of two pellets contained 22.6% and 22.8% of the heavy metals as plutonium. All these observations indicate the homogeneity of the mixed oxide pellets.

About 80 g of this mixed oxide was shipped to Battelle Pacific Northwest Laboratory for testing. Results for their first 2 pellets[5] are given in Table 1. The densities of the sintered pellets fabricated at both PNL, about 94% TD, and at ORNL, 95% TD, were in good agreement.

ORNL-DWG 82-55

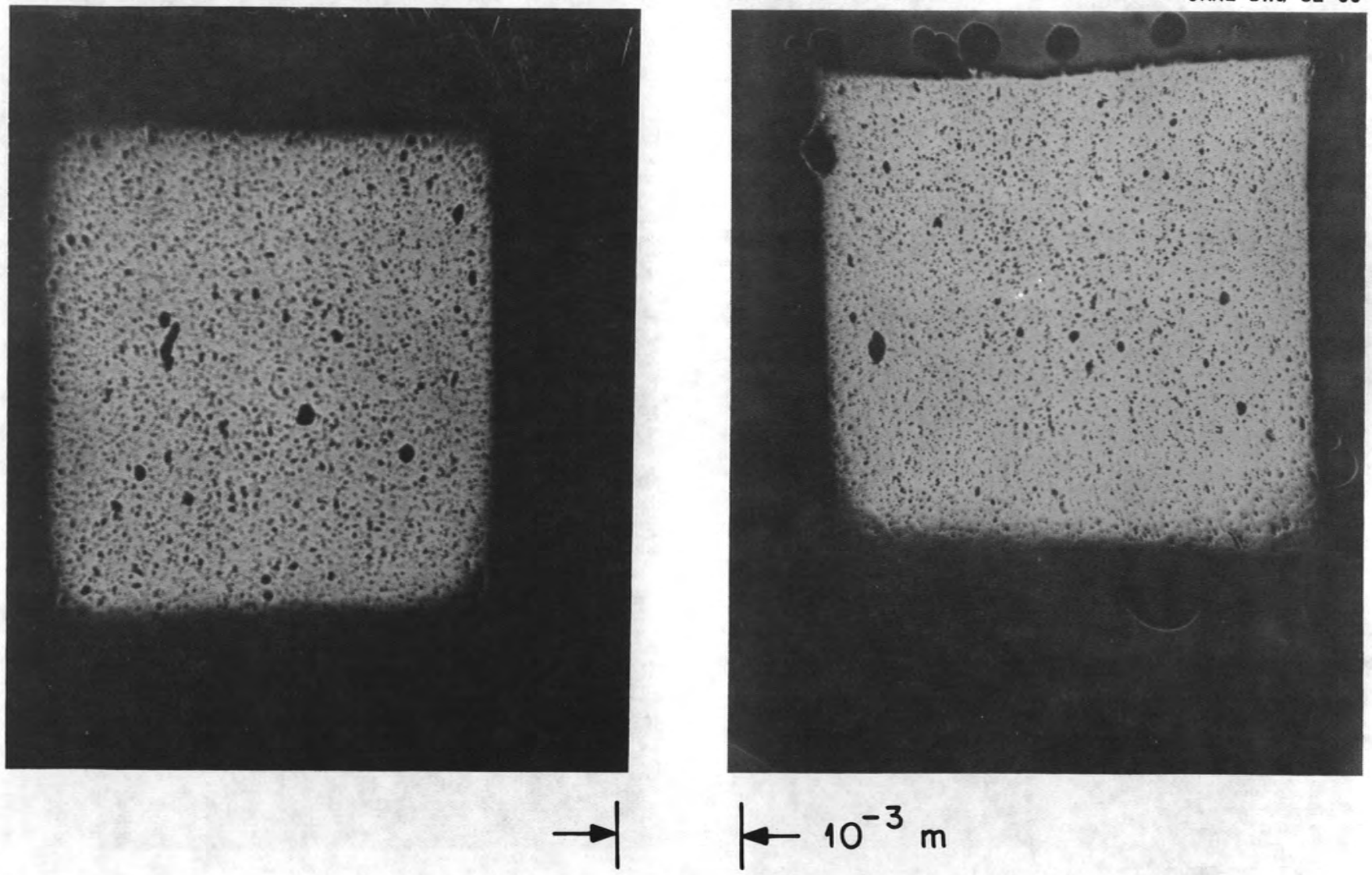

Fig. 2. Sintered pellets from first batch of mixed oxide powder.

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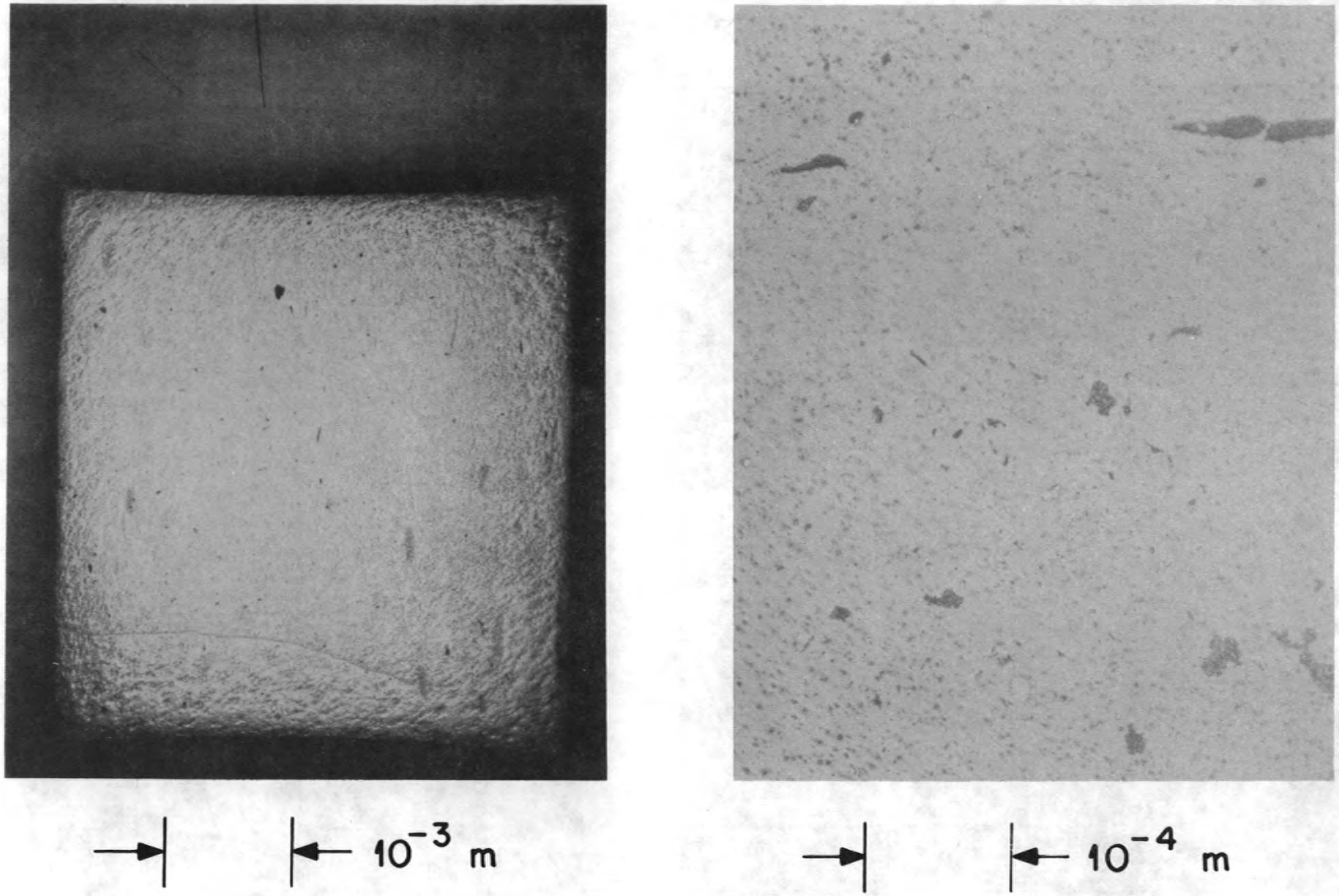

Fig. 3. Sintered pellet pressed from second batch of mixed oxide powder.

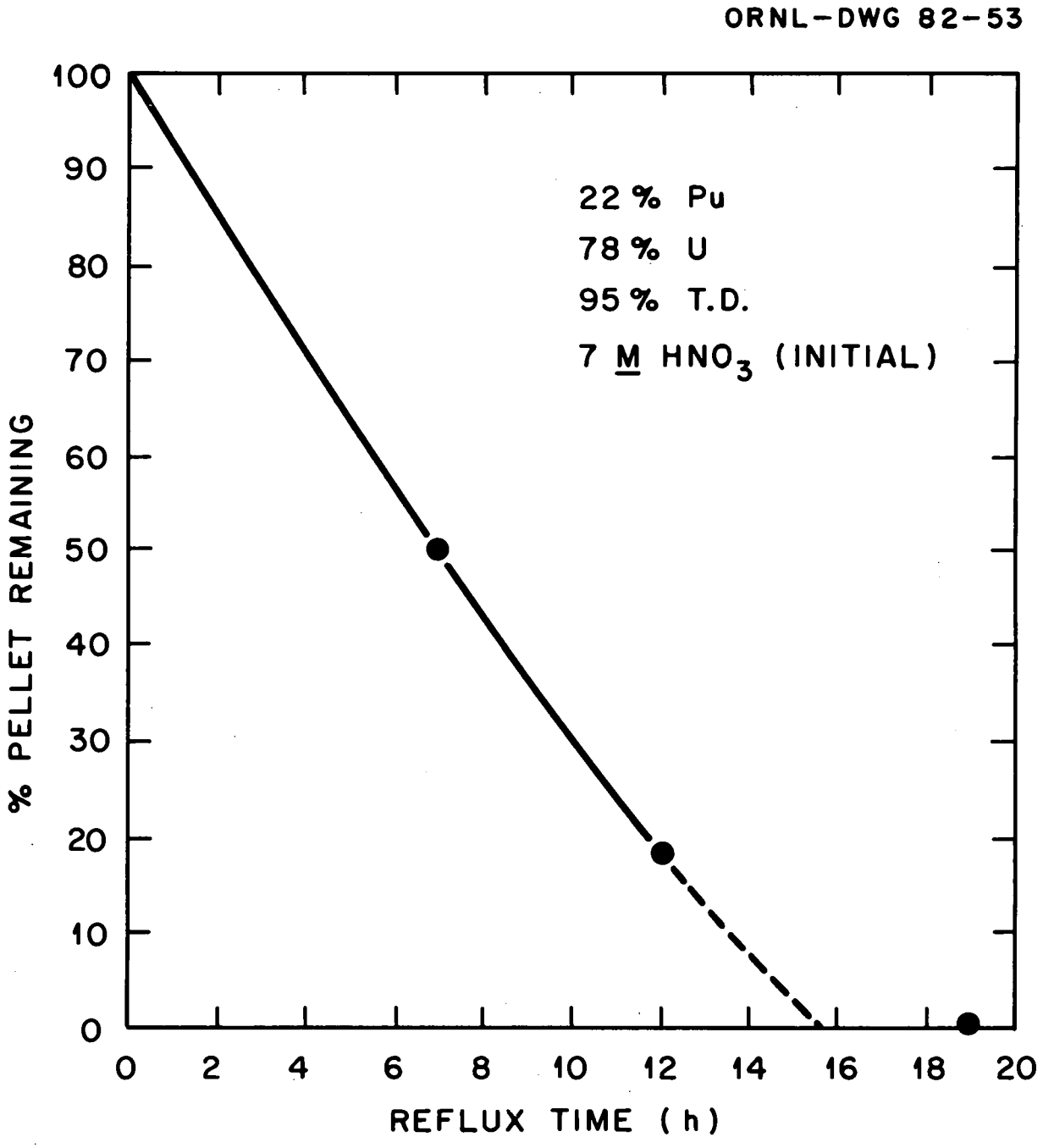

Fig. 4. Dissolution of sintered pellets of thermally denitrated mixed oxide.

Table 1. Fabrication properties for mixed oxide powder tests performed at PNL

As received		Calcining conditions		Calcine properties			Pellet properties[a]		
Tap density (g/cm^3)	Surface area (m^2/g)	Temperature (°C)	Time (h)	Weight loss (%)	Tap density (g/cm^3)	Surface area (m^2/g)	Forming pressure (MPa)	Green density (g/cm^3)	Sintered density[b] (% TD)
1.23	9.2	600	4	13.6	1.22	10.2	269	5.39	93.9
							296	5.50	93.5

[a] Note: After calcining, this powder was preslugged to 4.7 g/cm^3 and granulated through a 14-mesh screen. 35.4 wt % of the granules were -14+20 mesh. The remaining particles were less than 20 mesh in size.

[b] Sintered at 1700°C in 4% H_2-Ar for 4 h.

2.5 Plutonium Studies

A thermal denitration experiment with a plutonium nitrate feed solution containing about 0.42 M Pu (100 g/L) and 2 mol of ammonium nitrate per mol of plutonium in about 1.1 M HNO_3 produced a pure PuO_2 powder. No problems in the operation of the rotary calciner were observed, indicating the absence of a mastic stage in the thermal denitration. In later tests, batch evaporation of the feed solution generated a granular precipitate which was probably an ammonium nitrate double salt similar to that found with uranyl nitrate.[1,3] The precipitate was not characterized due to termination of the project.

The standard calcination-reduction of the PuO_2 caused only a 1.4% weight loss; this is not surprising since the plutonium product in the thermal denitration is PuO_2, whereas the uranium product is UO_3. The low weight loss does indicate that the product did not contain large quantities of undecomposed ammonium or plutonium nitrates. The PuO_2 powder after calcination had poor flowability and was difficult to load into the pellet die; however, pellets were pressed from this powder at 241 MPa (35,000 psi). One such sintered pellet had a bulk density of 89% TD and contained scattered, relatively large porosities (Fig. 5). The plutonia powder was certainly sinterable, but investigation of other sintering conditions to produce an improved product would be advisable before direct denitration is used for production of plutonia to be blended with urania for fuel pellet fabrication.

3. DISCUSSION

The direct thermal denitration process using ammonium nitrate for the preparation of mixed oxides worked very well. The small rotary calciner successfully produced acceptable ceramic-grade mixed oxide powder with only very minor startup problems. It appears that ceramic-grade powder with 20 to 25% plutonium (and perhaps higher concentrations) can be produced using the same conditions developed for uranium-only oxide production. This is certainly an important observation since it will minimize the amount of process development with plutonium. The

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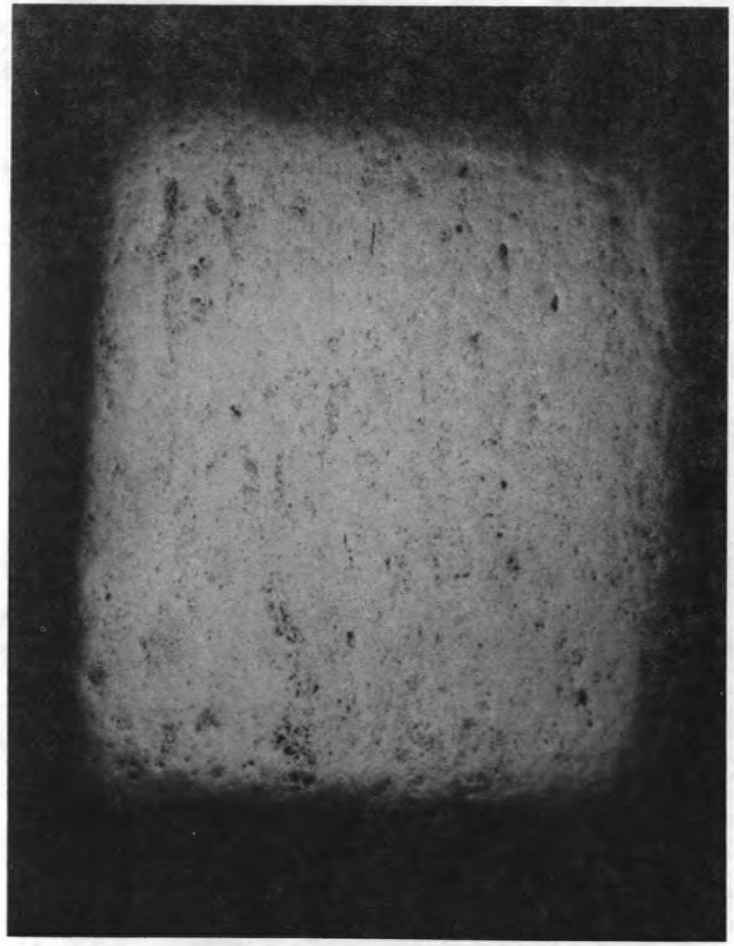
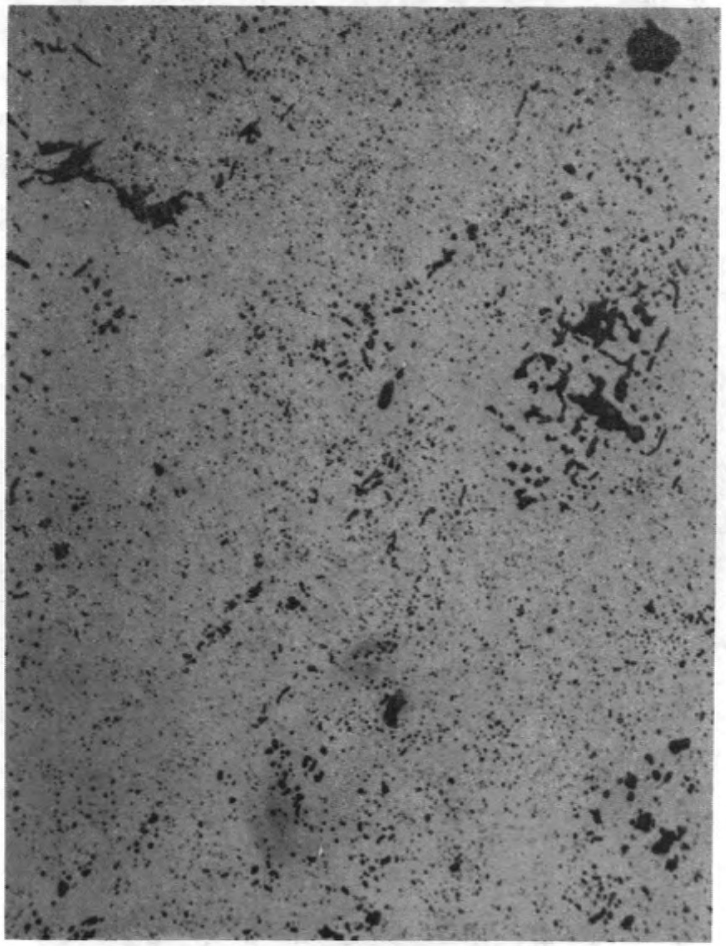


10^{-3} m



10^{-4} m

Fig. 5. Sintered pellet fabricated from PuO_2 powder prepared by thermal denitration.

addition of about 1 M free HNO_3 to the solution (the uranium-only tests have used essentially acid-free solutions) did not affect the quality of the powder. Additional testing, which was not done in this study because of fiscal restraints, should be undertaken to confirm that high-quality powder can in fact be produced consistently.

Sinterable PuO_2 was produced by this direct thermal denitration in one test, although the handling properties of the powder were unsatisfactory. Additional studies in this area are required to develop conditions for production of PuO_2 powder with satisfactory handling and ceramic properties.

4. ACKNOWLEDGMENTS

These studies were modeled as nearly as possible on the previous uranium oxide production studies of P. A. Haas. Powder reduction and pellet fabrication were performed in the ORNL Metals and Ceramics Division by W. B. Stines. Analyses of various solutions for uranium, plutonium, and various contaminants were performed by the ORNL Analytical Chemistry Division staff.

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