ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

DEVELOPMENT STUDIES ON A FLUIDIZED-BED PROCESS
FOR CONVERSION OF U/Pu NITRATES TO OXIDES

Part 1. Laboratory-scale Denitration Studies

by

S. Vogler, D. E. Grosvenor,
N. M. Levitz, and F. G. Teats

Chemical Engineering Division

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ABSTRACT

Laboratory experiments have been carried out to simulate the fluid-bed denitration of uranyl nitrate-plutonium nitrate solutions. These experiments indicated the denitration product to be UO_3-PuO_2 , which yielded UO_2-PuO_2 upon hydrogen reduction. From this UO_2-PuO_2 product, pellets of 89% theoretical density were prepared by sintering in argon at 1600°C. Electron microprobe examination of the pellets indicated good homogeneity with no evidence of isolated particles of plutonium oxide. The cosolubility of uranyl nitrate and plutonium nitrate (1-2M U + Pu) in nitric acid was measured. The invariant point was not reached for solutions containing 0.67 fraction plutonium

$$\left(\frac{Pu}{U + Pu} \right) .$$

INTRODUCTION

Conversion of uranyl nitrate and plutonium nitrate solutions (produced in reprocessing plants) to an oxide form is a necessary and presently an expensive step in the nuclear-fuel cycle for LMFBR fuels. This conversion must provide the fuel fabricator with powdered fuel oxides suitable for the fabrication of fuel shapes on a safe, reliable, economic basis. In addition, conversion of fissile nitrate solutions (including plutonium nitrate solutions) to a solid form is in itself of interest since a solid may be more easily and safely shipped than liquids.

Current conversion processes consist of a number of steps, among which are precipitation, filtration, and calcination. An alternative to these processes that offers potential economic advantages and uniform product is continuous fluid-bed denitration of uranium-plutonium nitrate solutions to a UO_3-PuO_2 powder form, followed by fluid-bed reduction to UO_2-PuO_2 . This denitration process is based on extensive fluid-bed denitration technology developed for uranyl nitrate and waste aluminum nitrate solutions.¹⁻³

An integrated program for laboratory studies and experimental work on a pilot engineering scale was set up. The program includes (1) calculational studies of the process scale-up potential for geometrically favorable column shapes such as slabs and (2) evaluation of UO_2-PuO_2 produced by denitration as fuel materials.

The laboratory program was directed toward a preliminary assessment of the fluidized-bed procedure for producing UO_2-PuO_2 powder of acceptable quality for the preparation of fuel pellets. Accordingly, the process steps were simulated on a laboratory scale. The laboratory studies included

(1) drop denitration of uranyl nitrate-20% plutonium nitrate feed solution, (2) hydrogen reduction of the denitration product, (3) pressing of pellets from the reduced oxides, and (4) sintering of the green pellets to yield the finished fuel pellet. The materials derived from steps 1, 2, and 4 were characterized by determination of their composition, structure, and homogeneity (distribution of the PuO_2 in the UO_3 matrix).

Auxiliary studies included:

1. Measurement of the solubility of uranium-plutonium nitrate solutions in the region of process feed interest, i.e., near 2.0M total metal ions including 20% plutonium.
2. Development of a procedure for dissolving mixed-oxide denitration products for reuse in the pilot-plant development program; redissolution of oxides minimizes plutonium inventory requirements.
3. Determination of the plutonium valence state after uranium-plutonium materials are dissolved and as the solution ages.
4. Determination of the effect of plutonium valence (IV and VI) upon the completeness of conversion to PuO_2 .

I. PREPARATION AND CHARACTERIZATION OF OXIDE POWDERS

A. Drop-Denitration Studies

Oxide powder was initially prepared by the laboratory-scale drop-denitration of uranyl nitrate-plutonium nitrate solutions. This material was examined and analyzed to help determine the effect of temperature of preparation upon product properties.

The drop-denitration experiments were carried out by allowing nitrate solution to drop into a quartz tube (2-in.-dia) held in an 8-in.-long vertical tube furnace. The tube was supported on a ceramic block which positioned the bottom of the quartz tube in the hot zone. The temperature was measured by a Chromel-Alumel thermocouple which passed up through the ceramic block and contacted the bottom of the quartz tube; the temperature was manually controlled by means of a Variac^{*} and was also recorded on a potentiometer recorder. A sufficiently slow drop rate was maintained so that each drop dried before the next drop fell.

1. Conversion of Uranyl Nitrate to UO_3

Preliminary denitration experiments with uranyl nitrate solutions were completed at 300, 400, 500, and 600°C to check out the laboratory-scale equipment and the procedure. The products all appeared the same (all were orange) with no visible evidence that the UO_3 was reduced to U_3O_8 or UO_2 .

X-ray diffraction examination of the product of uranyl nitrate denitration at 500°C showed that the product was gamma- UO_3 ; the product formed at 400°C consisted of gamma- UO_3 and $\text{UO}_3 \cdot \text{H}_2\text{O}$.

2. Conversion of Uranyl Nitrate-20% Plutonium Nitrate to UO_3 -20% PuO_2

After the preliminary experiments with uranyl nitrate solutions, the equipment was moved into a glovebox and denitration experiments were carried out at 300, 450, and 600°C with solutions containing 1.2M uranyl nitrate, 0.3M plutonium nitrate, and 2-4M nitric acid. Approximately 6 g of oxide was prepared in each experiment.

Examination by X-ray diffraction of the mixed oxide product prepared at 450°C indicated the major phase to be gamma- UO_3 . PuO_2 was reported to be a possible minor phase, although only a limited number of characteristic lines were observed.

The powder prepared at 450°C was further characterized by microscopic, electron-microprobe, and alpha autoradiographic examination.

a. Electron-Microprobe Examination

A sample of the oxide powder prepared at 450°C was introduced into a metallographic mount suitable for electron-microprobe examination.

^{*}Product of General Radio Co.

The material was polished, the final polish being with Linde A (alumina abrasive, 0.3- μ m diameter). After polishing, a 50Å coating of gold was sputtered on the sample surface to provide heat conduction and to prevent contamination of the equipment.

Before the microprobe examination, the particles were examined under the microscope. At a magnification of 100x, particle diameters varied widely. The particles exhibited a metallic luster and were irregularly shaped. Voids were apparent in many of the particles.

In the examination of a sample, the electron beam (0.5 μ m in diameter) was focussed initially on a spot in one of the particles. The characteristic X-rays emitted by the plutonium (M β) and the uranium (M α) were counted simultaneously (for a fixed period of time), using separate proportional counters. Counting of single points was repeated randomly across the area of the particle. The counting rates were corrected for background, and the uranium-to-plutonium count ratios were calculated. The constancy of this value is a measure of the microscopic homogeneity of the powder particles. These point count scans indicated that there were localized differences in concentration; the relative standard deviation for the U/Pu ratio was $\sim$ 30%.

The product was reexamined using the same electron beam diameter and the same time interval. However, instead of being focussed on a single spot, the electron beam was systematically swept over an 80 by 100- μ m area; count rates were taken at different areas of the particle. The results obtained by scanning the large area (80 by 100 μ m) indicated that the overall homogeneity was good, the relative standard deviation was only about 7.5%.

b. Autoradiography

With an autoradiographic technique the ionization produced in a cellulose nitrate film by plutonium alpha radiation from UO_3 - PuO_2 prepared by denitration at 450°C is used to measure the homogeneity of plutonium distribution.⁴ (The molecular structure of the cellulose nitrate is deformed by ionization when energy is transferred from the alpha particles.) The cellulose nitrate film is subsequently placed in a sodium hydroxide solution, where the deteriorated area is attacked and removed, leaving cone-shaped voids that form an image.

In the preparation of an autoradiograph, first the UO_3 - PuO_2 powder sample is mixed with a plastic that sets at room temperature to form a casting with a 1-in. diameter. When the casting has hardened, it is polished in the same manner as the specimen for electron-microprobe examination. After polishing, the casting is wrapped in 1-mil Mylar to prevent any contamination by plutonium. A cellulose nitrate sheet ($\sim$ 1 in. square) is placed on the surface of the casting, with a single thickness of Mylar between the powder and the cellulose nitrate film. The cellulose nitrate is exposed to the alpha radiation for 1 min while a heavy weight on the cellulose nitrate provides close contact of the cellulose nitrate and powder. After the exposure, the cellulose nitrate is placed in 6.25M NaOH at 50°C for 4 min and then washed with distilled water. After air-drying, the cellulose nitrate is examined microscopically.

Qualitative inspection of the film indicated that plutonium distribution in the powder is rather uniform. These results confirm the data obtained by electron-microprobe examination.

3. Conversion of Plutonium Nitrate to PuO_2

To obtain comparative data, denitration experiments were also performed with plutonium nitrate solutions. In preparation for the denitration experiments, a solution dilute in plutonium and nitric acid was concentrated by heating almost to dryness, then diluting the residue with dilute nitric acid. It is known that heating plutonium solutions containing nitric acid results in oxidation of some of the plutonium from Pu(IV) to Pu(VI); spectrophotometric measurements of the plutonium nitrate feed solution indicated that 60% of the plutonium was present as the plutonyl ion. When this solution was drop-denitrated at 450 and 300°C, PuO_2 was the only oxide phase found.

The crystallinity of the powder was poor; the oxide prepared at 450°C was more crystalline than that prepared at 300°C. The poor crystallinity resulted in diffuse diffraction lines, which made calculation of lattice parameters difficult.

In concentrated plutonium solutions containing approximately 2M nitric acid, the plutonyl ion is reduced to the tetravalent state under the influence of the plutonium alpha radiation (see section III.C.). A solution was allowed to stand until only tetravalent plutonium was present. Denitration was performed again at 300°C. The PuO_2 prepared in the latter case was more crystalline than the PuO_2 prepared earlier, but no other difference in the X-ray diffraction pattern was apparent.

In summary, only PuO_2 is formed when plutonium nitrate solution is denitrated at 300–450°C; also, the plutonium valence has no apparent effect upon the product characteristics. This is not too surprising since Drummond and Welch⁶ have shown that heating of $\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ crystals leads ultimately to the formation of PuO_2 at 220°C, although an intermediate product (which was taken to be a basic plutonyl nitrate) was believed formed.

B. Hydrogen Reduction of $\text{UO}_3\text{-PuO}_2$ to $\text{UO}_2\text{-PuO}_2$

The denitration of uranyl nitrate-plutonium nitrate solutions produces $\text{UO}_3\text{-PuO}_2$, which must be reduced to $\text{UO}_2\text{-PuO}_2$ before pellets are made. Prior fluidized-bed experience⁷ had indicated that reduction of UO_3 with hydrogen at ~550°C is feasible. Thermogravimetric (TGA) data⁸ showed that in the reaction of UO_3 with hydrogen, reduction starts at approximately 400°C and is complete at 500°C.

Exploratory reduction experiments were carried out in a tube furnace installed in a helium-atmosphere glovebox on $\text{UO}_3\text{-PuO}_2$ powder prepared by drop-denitration of a solution (containing about 1.65M total U + Pu) at 300°C. The $\text{UO}_2\text{-20 wt % PuO}_2$ product was intended for exploratory pellet fabrication and preliminary characterization tests.

Reduction was carried out at 550 and 500°C in a small stainless steel boat with approximately 6 g of $\text{UO}_3\text{-PuO}_2$ per experiment. The reaction

time was 4 hr, and the hydrogen flow rate was 100-200 cm³/min. Preliminary data indicate that reduction was at least 95% complete in both experiments.

The extent of reduction was determined by measuring the oxygen content of the product. However, the tube-furnace was opened in an impure helium atmosphere, making it possible that the oxide had reacted with the oxygen content of the box atmosphere. Thus the indicated reduction is a minimum value. Further reduction studies await engineering denitration studies with uranyl nitrate-plutonium nitrate solutions.

II. PREPARATION AND CHARACTERIZATION OF $\text{UO}_2\text{-PuO}_2$ PELLETS

A. Pelleting and Sintering

The purpose of these experiments was to determine whether $(\text{U,Pu})\text{O}_2$ prepared by denitration and reduction could be fabricated into good quality pellets, i.e., pellets with reasonably high densities and homogeneous distribution of the plutonium. Initial work explored briefly the effects of fabrication conditions on density. In the first preparation, as-produced $\text{UO}_2\text{-20 wt \% PuO}_2$ powder derived from drop-denitration at 300°C and hydrogen reduction at 550°C was pressed into 1/4-in.-dia pellets at 87,000 psi and sintered at 1650°C for 90 min. Sintering was carried out in an argon atmosphere. Physical measurement indicated that 84% of the theoretical density (T.D.) was achieved.

Several additional pellets were fabricated to explore briefly the effects of fabrication conditions with the objective of achieving a higher pellet density. Four $\text{UO}_2\text{-20 wt \% PuO}_2$ pellets were made from -100 mesh powder produced by drop denitration at 300°C and hydrogen reduction at 500°C (rather than 550°C). Two of these pellets were pressed at 87,000 psi; the other two were prepressed at 1500-psi pressure, granulated, and finally pressed at 87,000 psi. One pellet from each of the above pairs was sintered at 1650°C for 4 hr; the other two pellets were sintered at 1750°C for 90 min. The operating conditions and results for all pellet tests are summarized in Table 1. Prolonged heating at 1650°C did not increase the density. The pellet that had been prepressed, granulated, pressed, and sintered at 1750°C had the highest density--89% of theoretical. The density of the companion pellet, which had been pressed without granulation and sintered at 1750°C, was 83% of theoretical. Use of a lower temperature, 500°C instead of 550°C, for hydrogen reduction appeared to have no adverse effect on final pellet density.

From these preliminary results, we are optimistic that satisfactory fuel pellets can be prepared from this type of $(\text{U,Pu})\text{O}_2$ powder by the selection of appropriate pelletizing and sintering conditions.

B. Examination of $\text{UO}_2\text{-PuO}_2$ Pellets

The $(\text{U,Pu})\text{O}_2$ pellets were examined for composition, homogeneity, and structure.

TABLE 1. Operating Conditions and Results of $\text{UO}_2\text{-PuO}_2$ Pellet Fabrication Tests

Run No.	Initial Powder Mesh Size	Prepressing Pressure (psi)	Granulated Powder Mesh Size	Pressing Pressure (psi)	Green Density (g/cm^3)	Sintering Temp. ($^{\circ}\text{C}$)	Sintering Time (min)	Pellet Dia (in.)	Pellet Length (in.)	Final Density (g/cm^3)	% of T.D.
87 ^a	b	None	c	87,000	6.2	1650	90	0.252	0.282	9.3	84
89A ^d	-100	None	c	87,000	5.9	1650	240	0.248	0.203	9.3	84
89A ^d	-100	~1500	-45	87,000	6.1	1650	240	0.249	0.195	e	e
89B ^d	-100	None	c	87,000	5.9	1750	90	0.250	0.102	9.2	83
89B ^d	-100	~1500	-45	87,000	6.2	1750	90	0.246	0.166	9.85	89

^aThe $\text{UO}_2\text{-PuO}_2$ powder was prepared by drop denitration at 300°C followed by hydrogen reduction at 550°C .

^bNot measured.

^cNo granulation step used in these experiments.

^dThe $\text{UO}_2\text{-PuO}_2$ powder was prepared by drop denitration at 300°C followed by hydrogen reduction at 500°C .

^eNot measured because the pellet was chipped and cracked.

1. Chemical Analysis

One pellet having a density of 84% of theoretical (Table 1, Line 2) was used for analysis. One piece of this pellet was reserved for electron microprobe examination, and fragments of the second piece were analyzed for oxygen, uranium, and plutonium. The oxygen content was determined by vacuum fusion, and the uranium and plutonium concentrations were determined amperometrically. The results, summarized below, are within the current Fast Flux Test Facility (FFTF) specifications.⁹

U (wt %)	70.78 70.63	70.70
Pu (wt %)	17.61 17.60	17.60
O (wt %)	11.64 11.69 11.88	11.74
Oxygen/Metal Atom Ratio		1.98

2. X-Ray Examination

The lattice parameter for the pellet sample was 5.4602Å. This measured lattice parameter was compared with a value calculated from an equation derived by Schnitzlein.¹⁰ The equation applies to single-phase $\text{UO}_2\text{-PuO}_2$ and relates the O/M ratio, the lattice parameter, and the plutonium content of the $\text{UO}_2\text{-PuO}_2$.

$$a_o = 6.1127 - 0.534 (\text{Pu}) - 0.321 (\text{O/M}) + 0.229 (\text{Pu}) (\text{O/M})$$

where a_o is the lattice parameter, $(\text{Pu}) = \frac{\% \text{ Pu}}{\% \text{ Pu} + \% \text{ U}}$, and (O/M) is the oxygen to metal ratio. With two of the values known, the third may be calculated. The calculated value for a_o is 5.4610Å which compares very favorably with the experimental value of 5.4602Å (see following section). This agreement helps to confirm the presence of single-phase $\text{UO}_2\text{-PuO}_2$ in the prepared pellet. Only a single set of X-ray diffraction lines was in evidence, also indicating the presence of a single oxide phase.

3. Electron Microprobe Examination of $\text{UO}_2\text{-PuO}_2$ Pellets

The purpose of the electron microprobe examination of the pellets was to determine the homogeneity of uranium and plutonium distribution in the pellet. A section of a pellet was placed in a metallographic mount and polished suitably for electron microprobe examination. The final step was the deposition (by sputtering) of a 50Å coating of gold, which ensures adequate conduction and prevents contamination of the equipment.

Counting rates for a pellet sample were obtained with a 0.5-μm-dia beam of the electron microprobe by two procedures: fixed counting at randomly selected spots and scanning of 8- by 10-μm areas and 80- by 100-μm areas. Separate counting rates for uranium and plutonium were measured, and after correction for background, the uranium-to-plutonium counting ratio

was calculated. The constancy of this ratio is a measure of pellet homogeneity. Since the intensities of the characteristic uranium and plutonium X-rays are dissimilar, the absolute actinide content cannot be determined directly from the counting rates, except by the use of standards.

Twenty measurements of spots were made on various portions of the pellet. The data showed a spread of about 20%. Measurements also were made over many 8- by 10- μ m areas and 80- by 100- μ m areas for another series of measurements; no improvement in the dispersion of the data was observed. Nevertheless, these results are considered encouraging, since no spots or areas were found that contained only uranium or only plutonium. This series of measurements was made on an end face of the pellet. A second series of measurements, made close to the center of the pellet at randomly chosen portions of the pellet, corroborated that homogeneity was good and also gave data with improved statistics (relative standard deviation of 8-12%).

To further check the homogeneity of the pellet, complete scans with a 0.5- μ m-dia beam were made across a diameter of the pellet. In one such scan, successive 80- by 100- μ m areas were chosen that yielded 65 counting intervals. Every tenth interval was duplicated to check instrument performance. The uranium-to-plutonium ratio was calculated for each measurement, normalized to a standard UO_2 - PuO_2 pellet; the average value for the series of measurements was also calculated. The average U/Pu ratio was determined to be 4.00 with a relative standard deviation of 7.8%.

Each of the individual ratios was plotted as a function of its position along the pellet diameter (see Fig. 1). The results trace a sinusoidal curve, with the first 25% of the curve showing a greater variation than the remainder of the curve. The portion of the pellet scanned first had a severe crack; this may account for the greater scatter.

Individual uranium and plutonium X-ray counting rates were examined. Generally, both of these counting rates increased or decreased in unison, indicating the absence of appreciable localized enrichment (or, conversely, segregation) of either of the constituents.

In another test, a continuous scan with a 15- μ m-dia electron beam was made across the 0.25-in.-dia pellet, and the uranium and plutonium counting rates were continuously recorded. In this scan (Fig. 2), five divisions of the chart represent 1.5% of the diameter of the pellet. The scan shows that a change in the uranium counting rate was accompanied by a corresponding change (in the same direction) in the plutonium counting rates, indicative of a change in density rather than a change of concentration. A change in concentration would be indicated by a sharp increase in the counting rate for one of the actinides while the other decreased.

From the accumulated data obtained with the electron microprobe, it has been concluded that no segregation of PuO_2 occurred during pellet preparation and that homogeneity (plutonium oxide distribution in the UO_2 matrix) is good. The largest variation in plutonium counting rate, about 30% (from the highest to the lowest), represented a variation of plutonium content rather than segregation of PuO_2 . This variation, in part, may have been due to porosity or local density differences, since the electron

Fig. 1. Scan of a Diameter of a 0.25-in.-dia $\text{UO}_2\text{-PuO}_2$ Pellet with an Electron Microprobe (Data obtained with a 0.5- μm dia beam over successive 80 by 100- μm areas)

LiF Crystal
Pu(M β) 800 cps

ADP Crystal
U(M α) 4×10^3 cps

Fig. 2. Continuous Electron Microprobe Scan of a 0.25-in.-dia
UO₂-20% PuO₂ Pellet (5 chart divisions = 1.5% of pellet
diameter)

beam does penetrate the surface and the measurement is on a volume basis. A simple calculation showed that if a plutonium oxide particle completely filled an 8- by 10- μm counting area, the counting rate should increase by a factor of 4. Since the largest variation was 30%, any PuO_2 particles in the areas examined were significantly smaller than 10 μm .

It may be argued that large particles of PuO_2 may have been undetected. However, when spot or scanning measurements were made with the 0.5- μm beam, uranium and plutonium were always found with the proper amount of the complementary component. This is a further indication that not even a small degree of segregation occurs in this method of preparation.

The laboratory results to date show that drop denitration of uranyl nitrate-plutonium nitrate solutions yields a $\text{UO}_3\text{-PuO}_2$ powder which can be reduced to $\text{UO}_2\text{-PuO}_2$ and pressed and sintered into good-quality pellets. The highest density achieved was 89% of the theoretical density and the homogeneity of the plutonium oxide distribution in the uranium oxide matrix of each of these materials was good. Also, no segregation of plutonium occurs in the process. Further reduction and pelleting studies will be undertaken when material from the pilot plant denitration experiments is available.

III. SUPPORTING STUDIES

Although the primary aim of the laboratory studies was to demonstrate the suitability of the denitration process for producing homogeneous oxide powder from which fuel pellets could be made, other laboratory-scale experiments were performed in support of the engineering program.

A. Solubility Limits for U-Pu Nitrate Solutions

A knowledge of the cosolubility of uranyl nitrate and plutonium nitrate in dilute nitric acid is important to the selection of the feed composition for the fluid-bed denitration process. The feed solution should be as concentrated as possible to increase the throughput of the fluid-bed denitration reactors, but should not be so concentrated that inadvertent crystallization of plutonium nitrate (a criticality hazard) can occur. Since little crystallization data are available in the literature for uranyl nitrate-plutonium nitrate solutions with high plutonium contents, the temperatures at which solutions of given compositions begin to crystallize have been determined from cooling curves. The measurements were made on solutions in the range of process interest, i.e., 1 to 2M (U + Pu).

The procedure involved heating the test solution to approximately 5°C above the temperature of first crystallization and allowing the solution to cool slowly at a steady rate, with stirring. The solution temperature was measured with a stainless-steel-sheathed Chromel-Alumel thermocouple immersed in the solution and was recorded continuously on a strip chart recorder; the recorder traced a record of the solution temperature as a function of time. The onset of crystallization resulted in a decrease in the rate of the temperature change of the solution, because of the heat evolved during the crystallization process. The crystallization point was taken as the intersection of the two lines drawn through the two cooling-curve segments

representing different cooling rates.

The apparatus is singular in that the rate of cooling of the test solution (contained in a test tube projecting into a flask) was controlled by the flow rate of air cooled by dry ice located in the flask. The temperature measurements were corrected by measuring the temperature of an ice bath and also by measuring the freezing point of distilled water. Both methods gave the same reading, and a correction of -0.4°C was found to be required. Preliminary tests in which crystallization points were determined from cooling curves of uranyl nitrate solutions demonstrated good agreement of experimental results with the published data on uranyl nitrate solutions.

Ten test solutions were prepared from stock solutions of uranyl nitrate (2.52M), plutonium nitrate (1.5M), and concentrated nitric acid (16M). Approximately 30% of the plutonium was present as the hexavalent plutonyl ion. The crystallization point was determined two or three times for each solution. For solutions with a crystallization temperature greater than 10°C , the agreement for repeated measurements was always within 1°C . For crystallization temperatures below 10°C , agreement was within $\pm 1.5^{\circ}\text{C}$. The crystallization points of some test solutions of various compositions are summarized in Table 2. Effects of solution composition on crystallization temperature and on the crystallizing species are discussed below.

1. Effect of Acidity on Crystallization Temperature

The effect of nitric acid concentration on the crystallization temperature of plutonium nitrate-uranyl nitrate-nitric acid solutions is shown in Fig. 3. For reference, curves for the crystallization temperatures of uranyl nitrate-nitric acid solutions are included. The crystallization temperature for U + Pu nitrate solutions (total U + Pu of 1.4M and 1.6M; U/Pu = ~ 4) increased almost linearly in the acid range from 2 to 4M, but at a slightly lower rate than for uranyl nitrate alone. An acid increase from 2 to 3.4M increased the crystallization temperature by 12°C and 16°C for the mixed actinide and uranyl nitrate solutions, respectively. Beyond this point, the effect of acid concentration on crystallization temperature diminished. Increasing the acid concentration from 3.4 to 4.8M increased the crystallization temperatures of these solutions by only 5.6°C and 7.6°C .

2. Effect of Replacement of Uranium with Plutonium

The effect on crystallization temperature of replacing uranium with plutonium in plutonium nitrate-uranyl nitrate-nitric acid solutions was studied. Figure 4 shows that as the fraction of plutonium in the solution, $\frac{\text{Pu}}{\text{U+Pu}}$, was increased to 0.67 (for fixed nitric acid and fixed total heavy metal concentrations), the crystallization temperature decreased. For a total heavy metal concentration of 1.4M and with 3.4M nitric acid, the crystallization temperature decreased from $\sim 13^{\circ}\text{C}$ (for a solution containing uranium only) to -1.5°C for a solution having a plutonium fraction of 0.5 and decreased to -8.5°C for a solution with a plutonium fraction of 0.67 (see Fig. 4).

TABLE 2. Crystallization Temperatures in the
Uranyl Nitrate-Plutonium Nitrate-Nitric Acid System

Solution Composition				Crystallization Temp. °C
U	Pu	HNO_3	U/Pu	
1.6	0.2	2.0	8.0	13.2
1.6	0.3	2.0	5.3	15.9
1.6	0.4	2.0	4.0	18.0
1.4	0	3.4	-	12.6 ^a
1.28	0.34	2.0	3.8	3.2
1.28	0.34	3.4	3.8	15.3
1.28	0.34	4.8	3.8	20.8
1.12	0.28	3.4	4.0	10.2
1.12	0.28	4.8	4.0	17.6
0.98	0.42	3.4	2.3	5.3
0.70	0.70	3.4	1.0	1.5

^aExtrapolated from literature data on UNH solubility (i.e., from I. Dillon, Argonne National Laboratory, private communication, 1950).

Fig. 3. Effect of Nitric Acid Concentration on the Crystallization Temperature of Plutonium Nitrate-Uranyl Nitrate-Nitric Acid Solutions

Fig. 4. Effect of Increasing Plutonium Content on the Crystallization Temperatures for Uranium-Plutonium Solutions

Total Heavy Metal Concentration: 1.4M

HNO₃ Concentration: 3.4M

3. Effect on Crystallization Temperature of Increasing the Plutonium Concentration at a Constant Uranyl Nitrate Concentration

Crystallization temperature was measured at a constant uranyl nitrate concentration of 1.6M, a constant nitric acid concentration of 2M, and various plutonium nitrate concentrations. As expected, increasing the total metal ion concentration in the solution by adding plutonium nitrate to a uranyl nitrate solution increases the crystallization temperature (Fig. 5).

4. Effect of Plutonium Valence State Upon the Crystallization Temperature

When the test solutions were first prepared, the plutonium nitrate had been freshly concentrated and contained 30% hexavalent plutonium. Upon standing, hexavalent plutonium was reduced to the tetravalent state as a consequence of the intense alpha radiation. The crystallization experiments were repeated on the same solutions after they stood three months. Essentially the same crystallization temperatures were obtained as for the freshly prepared solutions, showing little or no effect of the plutonium valence state (at least the valence states examined) upon the crystallization temperature.

5. Identification of the Crystalline Phase

A phase rule analysis of the uranyl nitrate-plutonium nitrate-nitric acid system indicates it is probable that the crystallized phase on the uranium-rich side of the invariant point is uranyl nitrate hexahydrate. Because of the importance of ensuring that plutonium does not crystallize from solution, several experiments were carried out to identify the crystallized phase in solutions of process interest and to confirm the theoretical evaluation.

The procedure consisted of first crystallizing a fraction of the material from solution and separating the precipitate from the bulk of the solution by centrifuging and decanting. The crystallized material was then dissolved in 1M nitric acid, and the solution was analyzed for plutonium by alpha liquid scintillation counting. The uranium-to-plutonium ratio was determined by X-ray fluorescence analysis. This technique was favored over X-ray diffraction analysis because it was simpler and was specific for uranium and plutonium.

The results of tests with four uranium-plutonium solutions are summarized below.

Fig. 5. Effect on Crystallization Temperature of Adding Plutonium Nitrate to 1.6M Uranyl Nitrate-Plutonium Nitrate-2N Nitric Acid Solutions

Test No.	Starting Solution Composition, M		% of Original Pu in Crystallized Phase	U/Pu Ratio in Crystallized Phase
	U	Pu		
1	1.60	0.40	2.5	16.5
6	1.12	0.28	3.9	20.2
9	0.98	0.42	2.1	15.5
10	0.86	0.82	3.4	8.4

The crystallized phase from tests 1, 6, and 9 was yellow; the phase from test 10 appeared to be the same material but had a green cast. The crystallized phase from all four tests was assumed to be uranyl nitrate hexahydrate. The analyses confirmed that the solid was uranyl nitrate, even in the solution with a U/Pu ratio of one.

The plutonium associated with the crystallized phase is attributed to a sorption phenomenon. It is known that sorption of a second species occurs when a salt is crystallized from a solution containing more than one species. A sorption test was made with uranyl nitrate solution containing cesium-137 tracer to gain insight into this phenomenon. When approximately 10% of the uranyl nitrate had crystallized, 3.4% of the original cesium activity was found with the crystallized phase. Since the plutonium concentrations in the crystallized materials were at about the same level as the tracer, a similar mechanism was assumed responsible in both cases.

The data presented in Fig. 4 show that the invariant point for the uranyl nitrate-plutonium nitrate-nitric acid system lies on the plutonium-rich side ($Pu/U > 1$). A possible explanation for the plutonium content of the crystallized phase from test 10 being 12% as compared with 5-6% for the other tests (see tabulation above) may be merely that uranyl nitrate crystallized from a solution much more concentrated in plutonium. In test 10, the plutonium concentration was twice the concentration in the next most concentrated solution, and the increased density of plutonium ions made for easier occlusion and sorption of plutonium.

6. Discussion

The crystallization data reported above represent some of the points on the phase diagram of the uranyl nitrate-plutonium nitrate-nitric acid system and may be evaluated by the techniques of the phase rule. At a crystallization point, the system consists of two phases, a liquid and a solid; according to the phase rule, four degrees of freedom exist. Some of these may be fixed. In the example presented in Fig. 4, the pressure is atmospheric, the acid concentration is 3.4M, and the total metal concentration is 1.4M. Under these conditions, the system becomes univariant and as the plutonium content changes, there is a corresponding change of the crystallization temperature. If the precipitate is assumed to be uranyl nitrate hexahydrate (UNH), Fig. 4 shows the solubility line for a range of plutonium concentrations in equilibrium with solid UNH. There is a

corresponding curve for the solubility of uranyl nitrate in equilibrium with solid plutonium nitrate. These curves should intersect at the invariant point, where a fixed solution composition is in equilibrium with solid uranyl nitrate hexahydrate and solid plutonium nitrate. In these results, it appears that the invariant point has not yet been reached. The stability of plutonium nitrate in these solutions is probably a consequence of the formation of stable complex ions of plutonium (IV) ions and nitrate ions in nitric acid solutions.

The data are adequate for establishing the composition of feed solutions for future fluidized bed operations. A first approximation of the total actinide solubility can be obtained from the known uranium solubility data since the substitution of plutonium for uranium, at least to a plutonium fraction of 0.6, will result in an increased uranium plus plutonium solubility, manifested by a decrease in the crystallization temperature. The curves in Fig. 3 show that the U-Pu solutions are less sensitive to changes in nitric acid concentration than are uranium solutions. It is also apparent that the plutonium valence state (at least within the limits tested) has little if any effect on the crystallization temperature. Finally, measurement of the uranium and plutonium content of the crystallized phase demonstrated that it was largely uranyl nitrate with a slight amount of plutonium. This conforms to the phase rule evaluation. The composition of the crystallizing phase has not been determined but is most likely uranyl nitrate hexahydrate.

B. Dissolution of Oxide Produced by Denitration

Although dissolution of the $\text{UO}_3\text{-PuO}_2$ oxide is not a requirement of the denitration process, this step will allow fresh feed solutions to be prepared for the pilot plant by recycling the denitration product. Recycling will minimize plutonium inventory requirements in the glovebox.

Nitric acid dissolution experiments of a scoping nature were performed on a gram scale with $\text{UO}_3\text{-20% PuO}_2$ produced in laboratory drop denitration experiments. Since the rate of dissolution of the PuO_2 fraction is known to be limiting, the plutonium content of the solution was monitored (by liquid scintillation counting) as a function of time of dissolution. The first dissolution experiments were carried out at 95°C with concentrated nitric acid on powders prepared at 300, 450, and 600°C.

The procedure consisted of placing approximately one gram of the prepared oxide in a 40-ml centrifuge cone with 10 ml of concentrated nitric acid. The centrifuge tube was placed in a boiling water bath and the solution was stirred mechanically. After elapsed times of 0.5-hr, 2-hr, and 5-hr, stirring was stopped and the tube was removed from the water bath and cooled. A sample of the supernatant solution was taken after the undissolved oxide had settled. After 5 hr of stirring, the solution was then decanted and the undissolved oxide was completely dissolved in approximately 10 ml of concentrated nitric acid containing 0.05M HF. A sample of the latter solution was also taken. All of the samples were analyzed for plutonium. The data indicated that the $\text{UO}_3\text{-20% PuO}_2$ powder prepared at 300°C was most easily dissolved. Approximately 95% of the plutonium in this oxide dissolves in 2 hr to yield a solution 0.35M in heavy metals.

TABLE 3. Dissolution in Nitric Acid of UO_3 -20 wt % PuO_2 and PuO_2
Prepared by Drop Denitration

Expt. No.	Molarity of Starting Acid	Oxide Prepn. Temp. (°C)	Dissolution Temperature ^a (°C)	Molarity of Heavy Metals in Final Soln.	% Pu Dissolved in		
					0.5 hr	2.0 hr	5.0 hr
2	16	600	95	0.35	41	85	90
1	16	450	95	0.35	78	81	98
3	16	300	95	0.35	84	96	99
4	16	300	120	0.35	87	95.5	97.5
5	16	300	120	1.5	89	97	99.5
7	10	300	115	1.5	57.5	86	95
6	5	300	110	1.5	26	43	74 ^b
8 ^c	16	300	120	1.5	27	35	49
9 ^c	16	300	120	0.35	19	21	32

^aIn experiments 4 to 7, the temperature was the refluxing temperature of the acid concentration used.

^bAt the end of experiment 6, the solid residue was contacted with two additional acid aliquots for 2 hr each, dissolving an additional 15% of the plutonium. A final addition of concentrated nitric acid dissolved an additional 10% of the plutonium in 2 hr, leaving a residue of 1% of the plutonium.

^c PuO_2 only.

Because of the better dissolution characteristics of UO_3 -20% PuO_2 produced at the lower temperature (300°C), experimentation continued with this material. These additional experiments examined the effects of acid concentration and dissolution temperature on the rate of dissolution. Results for mixed oxide were also compared (Table 3) with results for the dissolution at 120°F of PuO_2 prepared by drop denitration. Plutonium material balances for these experiments ranged from 90-95%.

Data indicated (1) that mixed oxide prepared at higher temperatures was more difficult to dissolve, (2) that the rate of oxide dissolution was not affected significantly by the dissolution temperatures, (3) that the dissolution rate was not affected by a higher final actinide concentration when dissolution was with 16M nitric acid, and (4) that the fraction of plutonium dissolved was greater at the higher acid concentration. Also, plutonium in the UO_3 - PuO_2 material dissolved more rapidly than pure plutonium oxide (99% in 5 hr for Expts. 4 and 5 as compared with 30-50% in 5 hr in Expts. 8, 9). Despite this problem, it may be possible to recycle plutonium oxide in the pilot plant facility by redissolving most of the oxide and allowing a heel to remain in the dissolution vessel.

To verify that dissolution of UO_3 is rapid, several dissolution experiments were performed with UO_3 prepared in a fluidized-bed reactor in an earlier investigation. With a dissolution temperature of 95°C and sufficient oxide to yield a 1.5M uranium solution, the oxide was completely dissolved in less than 5 min with either 16 or 5M nitric acid.

A final experiment was carried out with approximately 4M nitric acid at room temperature. The volume and concentration of acid were chosen to yield a final solution 1.5M in uranium and 1M in nitric acid. In 20 min, the reaction was almost complete, and after 30 min of reaction at room temperature the oxide was completely dissolved.

From these laboratory data, a tentative procedure for carrying out dissolution in the pilot plant has been developed. This procedure takes advantage of the ready solubility of the UO_3 fraction in 3M nitric acid. The uranium-bearing solution would be transferred to a reservoir, and the PuO_2 heel would then be dissolved in 16M nitric acid. Little, if any, material would remain undissolved as a heel in the dissolution vessel.

A laboratory experiment (experiment 10) was performed to test the feasibility of this procedure. Initially, a 2.95 g sample of UO_3 -20 wt % PuO_2 (prepared at 450°C) was mixed with 8 ml of 3M nitric acid for 1 hr at room temperature. After the residue settled, the supernatant solution was decanted. Then approximately 8 ml of 16M HNO_3 was added to the residue, and dissolution was continued at 95°C with stirring. Samples of the new supernatant solution were taken after 1/2, 2, and 5 hr of stirring. For material balance purposes, the supernatant was decanted after 5 hr of dissolution. The residue was dissolved in 16M nitric acid containing 0.05M HF, and this solution was sampled. All of the samples taken during the dissolution experiment were analyzed for plutonium by liquid scintillation counting. The results are summarized in Table 4.

TABLE 4. Dissolution of $\text{UO}_3\text{-PuO}_2$
(Oxide prepared by denitration at 450°C)

Operation	Time (hr)	Experiment 10 ^a		Experiment 1 ^b
		Pu Dissolved (%)	Cumulative Pu Dissolved (%)	Cumulative Pu Dissolved (%)
UO_3 Dissolution	1	14	14	
PuO_2 Dissolution	1/2	45	59	78
	2	29	88	81
	5	1	89	98
Residue Dissolution		11		100

^aThe conditions of the dissolution are given in the text.

^bThe oxide was dissolved directly in 16M nitric acid at 95°C .

Approximately 14% of the plutonium in the mixed oxide dissolved with the bulk of the uranium in 3M nitric acid. In the second part of the test, after 1/2 hr at 95°C a total of 59% of the plutonium had dissolved; after 2 hr, 88% had dissolved; and after 5 hr, 89% had dissolved. For comparison purposes in Table 4, results are included from an experiment (experiment 1) in which the same mixed oxide was dissolved directly in 16M nitric acid at 95°C. The results of Experiment 10 agree reasonably well with the results of the direct dissolution experiment.

Analyses of solutions from Experiment 10 for uranium indicated that about 70% of the uranium dissolved in the 3M nitric acid and about 30% dissolved in the 16M nitric acid. Application of heat to the 3M nitric acid dissolution would be expected to improve the uranium dissolution rate and may dissolve additional plutonium.

C. Stability of Plutonium Ions in Solution

The valence distribution of plutonium ions in nitrate solutions is of interest in this program, since it might affect the oxide product formed upon denitration of such solutions. The plutonium nitrate used in our experiments was derived by the dissolution of PuO_2 in hot concentrated nitric acid, and hot nitric acid is capable of oxidizing tetravalent plutonium to hexavalent plutonium. Spectrophotometric measurements indicate that immediately after preparation, our plutonium solutions contain as much as 60% hexavalent plutonium.

It is known that in concentrated aqueous plutonium solutions, the alpha activity is intense enough to cause reduction of hexavalent plutonium to tetravalent plutonium, probably through the formation of peroxides.¹¹ Early data show that the reduction rate of Pu(VI) is of zero order.¹²

A zero order reduction of Pu(VI) was confirmed by experiments with ^{238}Pu .¹³ In tests in which the plutonium concentration was kept constant and the fraction of ^{238}Pu varied between 0.2 and 0.8, it was demonstrated that the rate of reduction decreases as the alpha activity decreases.

The change in valence distribution of plutonium ions in nitrate solutions with time was measured by spectrophotometric examination of a 3M HNO_3 solution containing 1.35M plutonium. This solution was sampled at intervals of several days, and the amounts of Pu(VI) and Pu(IV) were calculated from the optical spectra. Figure 6 presents our results along with data from Atlantic-Richfield, Hanford¹⁴ for 5.3M HNO_3 solution containing 0.82M Pu . To allow comparison with results when uranyl nitrate is present, three data points obtained in earlier ANL work for a 2-4M HNO_3 solution containing 1.2M $\text{UO}_2(\text{NO}_3)_2$ and 0.3M Pu are also included in Fig. 6. The plots show a straight-line relationship for the concentration of Pu(VI) as a function of time in the early part of the reaction, indicating a zero-order reaction rate with respect to the Pu(VI) concentration. The slopes for the two plutonium solutions are similar, indicating that the rate of valence change is independent of the initial plutonium concentration in this range. After about 50 days, the rate of reaction in the ANL solution increased.

Fig. 6. Reduction of Pu(VI) in HNO_3

No spectra for trivalent or pentavalent plutonium were observed for the 3M HNO_3 solutions containing 1.35M plutonium.

To relate the reduction rate of hexavalent plutonium solutions to the alpha activity of the solutions used, alpha activities were calculated and tabulated below.

<u>Source of Solution</u>	<u>Alpha Activity</u> <u>[disintegrations/(min)(ml)]</u>
Atlantic-Richfield Plutonium Solution	5.06×10^{10}
ANL Plutonium Solution	4.77×10^{10}
ANL Uranium-Plutonium Solution	1.84×10^{10}

The alpha activities for the Atlantic-Richfield solution and the ANL plutonium solution were similar, explaining the similarity in the rates of reduction (Fig. 6). The uranium-plutonium solution has too few data points for a good comparison, but it does appear that the initial rate of reduction was lower than that for the plutonium solutions.

These data confirm the results of other investigators who observed that hexavalent plutonium is reduced under the influence of plutonium alpha radiation with a zero order reaction rate.

IV. CONCLUSIONS

1. On the basis of these laboratory experiments, it is expected that fluid-bed denitration of uranyl nitrate-plutonium nitrate solution will yield a homogeneous $\text{UO}_3\text{-PuO}_2$ product. Results also indicate that after reduction of this powdered oxide to $\text{UO}_2\text{-PuO}_2$, fuel pellets of suitable homogeneity can be fabricated.

2. The $\text{UO}_3\text{-PuO}_2$ oxides produced by denitration have adequate solubility and rates of solution in nitric acid so that a given amount of plutonium may be continually recycled through the equipment during the experimental program.

3. The cosolubility of uranyl nitrate-plutonium nitrate in nitric acid solutions comparable to expected process solutions was measured. The replacement of uranyl ions with plutonium ions increases the total metal solubility, which provides a greater flexibility in choosing feed compositions.

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