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CONVERSION OF URANIUM NITRATE TO CERAMIC-GRADE OXIDE FOR THE LIGHT WATER BREEDER REACTOR: PROCESS DEVELOPMENT

J. M. Leitnaker
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OAK RIDGE NATIONAL LABORATORY
operated by
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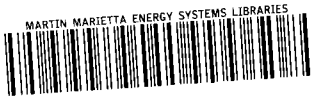

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CONVERSION OF URANIUM NITRATE TO CERAMIC-GRADE OXIDE FOR THE LIGHT WATER BREEDER REACTOR: PROCESS DEVELOPMENT

J. M. Leitnaker M. L. Smith[1]
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ABSTRACT

A limited study was made of an "ADU" process to make UO_2 for use as fissile material dissolved in ThO_2. A factorial study of precipitation included measuring the effects of initial nitric acid content of uranyl nitrate, the temperature of precipitation, the final pH of the solution, and time of digestion on the composition of the uranate cake and the surface area and tap density of the final powder. Studies of drying measured the effect of time, temperature, and grinding of the yellow cake on the surface area and tap density of the final powder. Effects of temperature and time were studied on the composition and surface area of "UO_3" made by heating ammonium uranate in argon. Effects on surface area of the temperature of reduction of uranate in H_2 were studied. Factors affecting stabilization of UO_2 powder were also studied, and the mechanism causing ignition of UO_2 was elucidated.

INTRODUCTION

The Light Water Breeder Reactor (LWBR) is to contain ThO_2 pellets in which from 1 to 6% $^{233}UO_2$ is dissolved. ORNL participation in the LWBR program, under contract with Bettis Atomic Power Laboratory (BAPL), involves:

1. the receipt and storage of several hundred kilograms of ^{233}U in various forms,
2. the purification of this material in the form of uranyl nitrate to remove ^{232}U daughters,
3. the conversion of the uranyl nitrate to ceramic-grade UO_2 powder,

[1]Co-op student from Virginia Polytechnic Institute and State University, Blacksburg, Va. 24060.

4. the packaging and shipping of the UO_2 to BAPL for blending with thoria and pressing into pellets, and
5. the recovery of ^{233}U from $^{233}UO_2$ scrap generated at ORNL and the $^{233}UO_2$-ThO_2 scrap generated at BAPL.

The Metals and Ceramics Division's responsibility has been the development of the chemical flowsheet to be used to convert the nitrate solution to a ceramic-grade UO_2 powder having the desired characteristics to permit uniform blending with the ThO_2 powder and pressing and sintering into high-density, homogeneous pellets. This report describes the development of this flowsheet and the investigation of the process limits of the various parameters involved in the flowsheet.

The basic flowsheet for the $^{235}UO_2$ production process involves: (1) dissolution of U_3O_8, (2) precipitation and separation of ammonium uranate cake, (3) drying the uranate cake, (4) reduction of the uranate cake to UO_2, and (5) stabilization of the UO_2. The first step involved selection of a particular flowsheet from among the choices available. A batch process was selected because of criticality as well as accountability considerations. Gaseous NH_3, which is easier to handle than a water solution and is usually cleaner, was chosen. The batch process made centrifuging the uranate slurry more attractive than filtration. Drying the uranate cake in a microwave oven avoided the necessity for handling the wet cake and generally simplified handling at this stage.

Because of the small batches used in the developmental study, the powder was reduced in a fixed rather than a continuous furnace. The dried, ground uranate was put into the furnace in boats and heated to a desired temperature in argon, and then hydrogen was admitted to serve as the reducing gas. After the furnace was cooled, the UO_2 powder was removed into an argon-filled glove box and then stabilized, in most cases mechanically. Developmental runs (involving $^{238}UO_2$) were often sampled for desired analyses before stabilization. In production runs (involving $^{235}UO_2$), the powder was always stabilized, homogenized in a V blender, and then sampled for desired analyses.

First, we established a tentative flowsheet, based both on experimental experience and literature reports on production of UO_2. Next,

to optimize the process, we investigated those production parameters that might affect the final product. This program was limited to: (1) providing the minimum information needed to determine the effects of changes in UO_2 process variables on $^{233}UO_2$ powder produced by ORNL for BAPL, and (2) ascertaining optimum limits on the variables from both cost and quality standpoints.

Ultimate evaluation of the final product involved testing $^{235}UO_2$ powder by blending it with ThO_2, pressing into pellets, and sintering to the desired density under conditions to be used with $^{233}UO_2$. Since not every powder produced in the developmental effort could be tested in this way, the procedure of choice was to evaluate the developmental powders by chemical analyses, surface area and tap density measurements, and scanning electron microscope observations and then choose representative conditions to produce powder for final evaluation by blending, pressing, and sintering.

The topics of this document are in chronological order of development rather than according to the process sequence. Our early experiments revealed that before we could study the effects of any earlier procedure on the final UO_2 powder we had to prevent the material from igniting upon removal from the furnace. Thus, stabilization was the first experimental objective. A successful, controlled reduction of the ammonium uranate was then necessary before meaningful conclusions could be drawn concerning the effects of varying either the drying or the precipitation procedures. Continuing the reverse order of operation from that point on was a logical consequence. Finally, we describe two studies undertaken after the original investigation was completed.

PREVIOUS INVESTIGATIONS

The literature on the production, properties, characterization, and use of uranium dioxide is voluminous. We made no serious attempt to examine any significant fraction of it. Two reviews served as useful

starting points: the USAEC-sponsored "Uranium Dioxide: Properties and Nuclear Applications"[2] and a more recent review by Woolfrey.[3]

The earlier review convers in a general way many processes and production procedures. The later review covers the process of our choice, preparation and calcination of ammonium uranates, in some detail. Topics covered included "the preparation of ammonium uranates by precipitation or solid-state reaction; the effects of preparation conditions upon the composition, structure, morphology, surface area, and filtration of ammonium uranates; the thermal decomposition and reduction of ammonium uranates; and the effect of calcination conditions on the physical properties of the resultant powder". Much of the review had direct applicability to our process.

STABILIZATION

Finely divided UO_2 powder is pyrophoric and will spontaneously ignite in air to form orthorhombic U_3O_8 (ref. 2, p. 67). As we will show, the pyrophoricity is caused by an initial rapid reaction of the powder on exposure to oxygen. If combustion is successfully prevented, UO_2 will still react slowly with oxygen and moisture from the atmosphere in which it is stored. To maintain the oxygen and moisture content of the powder at some desired value, it is necessary to stabilize the powder to prevent initial combustion and to prevent subsequent pickup of excessive oxygen and moisture.

Four types of stabilization were successfully employed: (1) control of surface area, (2) use of an additive (moisture), (3) use of dry ice, and (4) mechanical stabilization.

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[2] J. Belle, ed., Uranium Dioxide: Properties and Nuclear Applications, Naval Reactors, Division of Reactor Development, USAEC, U.S. Government Printing Office, Washington, 1961.

[3] J. L. Woolfrey, The Preparation and Calcination of Ammonium Uranates – A Literature Survey, AAEC/TM-476 (September 1968).

Behavior of UO_2 in Dry Air or Oxygen at Low Temperatures

In order to understand the action of the various methods of stabilization, it is helpful to understand the basic behavior of UO_2 powder. Roberts[4] has shown that between −180 and 50°C an initial rapid chemisorption of oxygen takes place on UO_2 powder in which at least half the U^{4+} sites on the surface react with oxygen molecules. Ferguson and McConnell[5] have measured the quantity of heat released when freshly reduced UO_2 is exposed to oxygen at −183°C. The results on their sample UL-17 indicate that if the oxygen is admitted in small increments, 24.3 kcal of heat is released per mole of oxygen chemisorbed at "100% chemisorption." (Note that in Table 1 of Ferguson and McConnell,[5] the sixth increment should be changed from 0.18 to 0.48 cal evolved). Sample UL-12 evolved 25.2 kcal/mole oxygen chemisorbed at 91% chemisorption, and sample UL-19 evolved 28.7 kcal/mole of oxygen at 100% chemisorption. On one large-particle sample 32 kcal/mole of oxygen was evolved at just over 100% chemisorption when the oxygen was added in one increment. Following the rapid chemisorption, a slow oxidation takes place at room temperature (and up to 50°C), in which the weight gain initially is linear in the logarithm of time.[6] However, after about 300 hr, the weight gain is clearly no longer linear in the logarithm of time but rather increasing in rate.

Behavior of UO_2 in Dry Air or Oxygen at High Temperatures

Alberman and Anderson[7] studied the oxidation of UO_2 in air between 130 and 180°C, finding a quite different process than that occurring at

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[4]L.E.J. Roberts, "The Oxides of Uranium: Part V. The Chemisorption of Oxygen on UO_2 and on UO_2-ThO_2 Solid Solutions," J. Chem. Soc. 1954, 3332–3339.

[5]I. F. Ferguson and J. D. McConnell, "Heat of Adsorption of Oxygen on Uranium Dioxide at 183°C," Proc. Roy. Soc. (London) Ser. A, 241, 67–69 (1957).

[6]M. L. Smith and J. M. Leitnaker, Atmospheric Contamination of Uranium Dioxide Powder, ORNL-4704 (June 1971).

[7]K. B. Alberman and J. S. Anderson, "The Oxides of Uranium," J. Chem. Soc. 1949, S303–311.

lower temperatures; the high-temperature oxidation appears to be diffusion controlled.

Perhaps of greater interest to this study is the ignition temperature. Our experiments showed that heating UO_2 powder with a surface area of 8 to 10 m^2/g to just over 80°C in the boats we used caused ignition. We determined the ignition temperature of previously stabilized UO_2 in air more carefully by heating a sample (surface area: 4.2 m^2/g) in the bottom of a jar that was surrounded by a heated sand bath.

The temperature of the UO_2 powder was monitored as a function of time, and the time at which the first black spot appeared on the surface of the powder was noted. (Blackening indicates rapid oxidation to a higher oxidation state.) The data plotted in Fig. 1 indicate an ignition temperature of 70°C. The ignition temperature probably depends to some extent on particle size and perhaps on the size distribution.

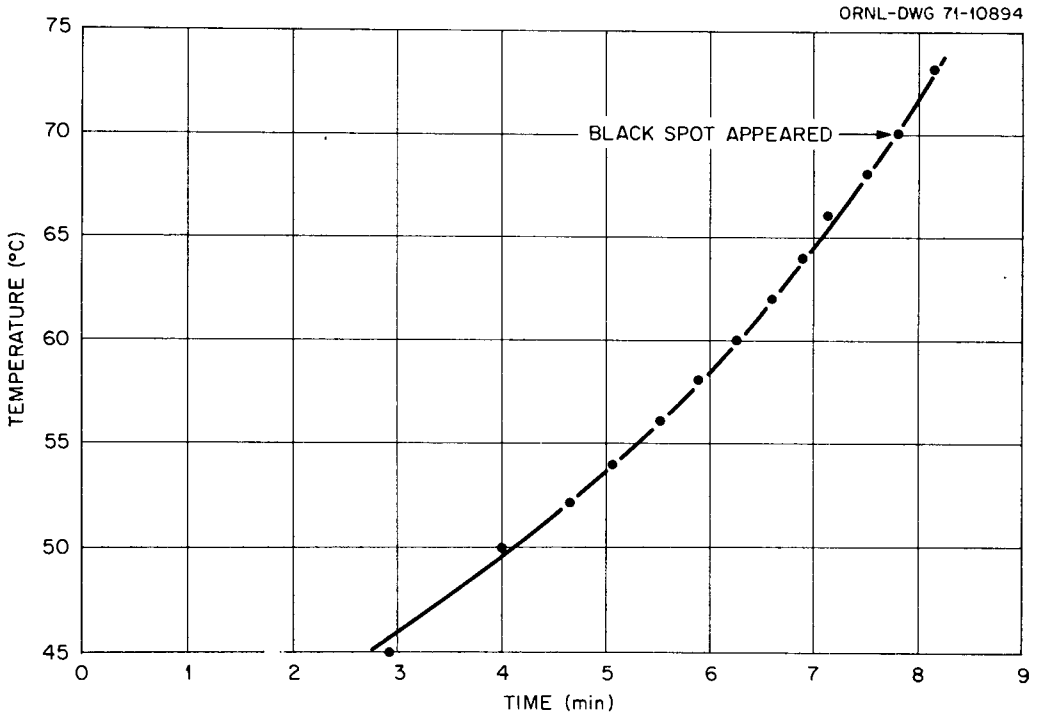

Fig. 1. Test of Burning of Previously Stabilized UO_2.

Behavior of UO_2 in Moist Air

Uranium dioxide adsorbs moisture from the air at a rate that depends on both the partial pressure of water and the surface area of the powder.[5,6] The shapes of the weight gain curves are similar to the room-temperature oxidation curves of the UO_2 powder described in the previous section. Pickup of moisture has no measurable effect on the rate of oxidation.[6] A saturation point is reached, depending on the partial pressure of H_2O, after which no further water is sorbed.

Stabilization of UO_2 by Control of Surface Area

The rapid initial adsorption of the oxygen on UO_2 is undoubtedly responsible for its ignition. However, we have observed that powders with surface areas up to 9 m^2/g do not ignite when exposed directly to air in the furnace boats we used.

To better understand what happens when freshly reduced UO_2 is exposed directly to air at 23°C, we performed several simple experiments. We put freshly reduced UO_2 (surface area = 4.2 m^2/g) in a 2.5-in.-ID screw-topped jar under argon. We took the jar into the air, removed the lid, inserted a thermocouple into the powder, and recorded temperatures and times.

In experiment 1 the sample was 1 in. deep, and the thermocouple was used as a stirring rod after 3 min exposure. The maximum temperature rise was about 16°C, which dropped rapidly on stirring. In experiment 2, the UO_2 was 1.6 in. deep, and the thermocouple was held steady at approximately the midpoint until an apparent maximum in temperature (30° rise) was reached; then the sample was stirred gently.

In experiment 3 the UO_2 was 2 3/4 in. deep, and the thermocouple was placed at a 1-in. depth. When the maximum rise (36°C) at this depth was reached and held for about 2 min, the thermocouple was thrust deeper in the powder to 2 in., whereupon the indicated temperature dropped. A second maximum was recorded: 26°C above the starting 23°C. This experiment is subsequently referred to as experiment 4. The data of all four experiments are plotted in Fig. 2.

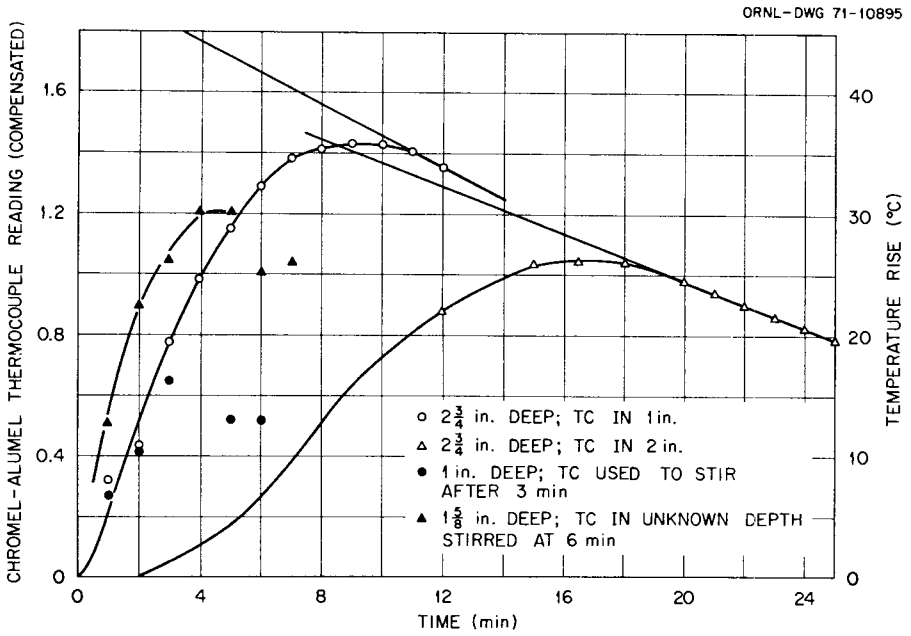

Fig. 2. Temperature Rise of UO_2 Exposed to Air. Experiment 1, ●; 2, ▲; 3, ○; 4, ▽.

The first two experiments should be regarded as preliminary. One can deduce that the temperature rise of the powder can be limited by gas movement.

Additional information can be deduced from the third and fourth experiments. These can be treated as crude calorimetric experiments, and heats for the overall process can be extracted from them. One can visualize the small volume of oxide surrounding the thermocouple as a calorimeter. Since the sample is constantly losing heat to the environment, a correction must be applied to calculate the temperature to which it would have risen. Hubbard et al.[8] detail several methods that can be applied to these results with appropriate accuracy. A "mid-time," T_m, of the experiment is defined such that:

$$T_m = T_f - \frac{1}{t_f - t_i} \int_{T_i}^{T_f} (t - t_i)\, dT , \qquad (1)$$

[8]W. N. Hubbard, D. W. Scott, and Guy Waddington, "Standard States and Correction for Combustions in a Bomb at Constant Volume," Chap. 5 in Experimental Thermochemistry, ed. by F. D. Rossini, Interscience, New York, 1956.

where t_f and t_i are the final and initial temperatures, respectively, of the heating period, and T_f and T_i are the corresponding final and initial times. For our experiment, the correction, Δt, to the temperature rise can be computed from:

$$\Delta t = \left(\frac{dt}{dT}\right)_f (T_f - T_m) , \qquad (2)$$

where $\left(\frac{dt}{dT}\right)_f$ is the cooling rate after t_f.

Application of these equations leads to a corrected temperature rise of 45.6°C for experiment 3 and 35.4°C for experiment 4. The error of these measurements in terms of corrected temperature rise is probably less a degree.

Another sample with a surface area of 7.0 m^2/g was tested (experiment 5) in the same general manner as the first four samples. A 1-in.-deep sample was used with a thermocouple at 0.5-in. depth. The temperature rose 83° in 5.0 min; burning on the surface was observed at 4.6 min. We conclude that a sample in a relatively thin layer may not be pyrophoric, but the same sample will ignite if arranged in a deep pile, since we observed powder up to 9 m^2/g did not burn in a furnace boat, in which the powder depth was approximately 1/4 to 3/8 in.

One can deduce that, when UO_2 is exposed to air, something other than a single, well-defined process is occurring. (The same conclusion is suggested in the experiments by Ferguson and McConnell[9] if one assumes the variation in their heat of chemisorption results is more than experimental error.) If only one surface layer were being chemisorbed on the powder and the same final state were reached in each case, the corrected temperature rise should have been the same in experiments 3 and 4; it was not. Further, one can arrive at a similar conclusion by considering the results of experiment 5 on powder with a surface area of 7.0 m^2/g.

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[9]I. F. Ferguson and J. D. McConnell, "Heat of Adsorption of Oxygen on Uranium Dioxide at 183°C," Proc. Roy. Soc. (London) Ser. A, 241, 67–69 (1957).

If one layer was chemisorbed, one could calculate the heat released and the maximum temperature rise. (This calculation assumes an area of 14.1 $Å^2$ for an oxygen molecule, while Roberts[10] uses 16.7 $Å^2$ for the effective area. We are really using the assumption that would result in the highest calculated heat release.) One surface layer would correspond to 2.27×10^{-2} moles O_2 chemisorbed per mole of UO_2. If one uses 30 kcal released per mole of oxygen chemisorbed,[9] one calculates the heat released at 669 cal/mole of UO_2. Taking the heat capacity of UO_2 as 16.5 cal $mole^{-1}$ $°C^{-1}$, a 40.5°C corrected temperature rise (to 63.5°C) should be observed. In fact, the temperature rose twice this amount within 5 min. (Note that this calculation assumes one complete monolayer is chemisorbed. Only a few of Ferguson's and McConnell's[9] samples chemisorbed oxygen corresponding to as much as 65% of a monolayer; most were between 25 and 35%.)

One might assume that the chemisorbed oxygen was diffusing into the UO_2 at the high temperatures, leaving a clean surface, which subsequently reacted. That this is probably not the case can be deduced from the experiments of Alberman and Anderson.[11] By extrapolation of their data to 63.5°C we calculate a diffusion coefficient of 1.1×10^{-19} cm^2/sec. Assuming the sample was at this temperature for 4 min (surely an upper limit), we calculate 3.69×10^{-4} moles O_2 per mole of UO_2 would diffuse into the interior of the particles. A temperature rise of less than a degree would result from chemisorption of this additional quantity of oxygen.

A reasonable explanation for the observed facts, without postulating any new mechanism, can be put forth by assuming a range of particle sizes in the sample. For example, suppose that the sample were made up of a mixture of two materials, with surfaces areas of 20 and 2 m^2/g, such that the average is 7.0 m^2/g. The material with a surface area of 20 m^2/g (27.8 wt %), if not cooled, would rise in temperature by 116°C

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[10]L.E.J. Roberts, "The Oxides of Uranium: Part V. The Chemisorption of Oxygen on UO_2 and on UO_2-ThO_2 Solid Solutions," J. Chem. Soc. 1954, 3332–3339.

[11]K. B. Alberman and J. S. Anderson, "The Oxides of Uranium," J. Chem. Soc. 1949, S303–311.

according to the same calculation method as above. If oxygen is readily available, this portion of the material could ignite and burn to U_4O_9, if we consider only the next stable higher oxide of uranium. The heat released for such a reaction,

$$UO_2 + 1/8\ O_2 \rightarrow UO_{2.25}\ , \qquad (3)$$

would be 10.5 kcal for each mole of UO_2, or 2920 cal assuming 27.8% of the material participated. This partial ignition would raise the temperature of the total mass by approximately 176°C, clearly enough to ignite the total mass if freely exposed to air with heat losses limited.

There is good reason to suppose that our UO_2 powder has a wide range of particle size. The section covering the scanning electron microscope examination of the powder will make this clear.

In summary, if UO_2 with a surface area of 7 m^2/g is exposed directly to the air, one should not expect the powder to ignite if the powder is rather uniform in size. On the other hand, if powder with the same surface area but containing a range of particle sizes is exposed to the air, ignition or lack of it would depend on whether or not the temperature was allowed to rise above about 70°C. Thus, Anderson et al.[12] observed that freshly reduced UO_2 powder with a surface area above 8.4 m^2/g was pyrophoric at room temperature, but oxide having a surface area below 2 m^2/g was not. If the higher-surface-area powder of Anderson were in a thinner layer, our data show that it would not have been pyrophoric Details of powder depth were not given by Anderson et al., nor was information on the particle size distribution.

Stabilization by Addition of Moisture

Uranium dioxide powder can be stabilized by passing a gas – for example, cracked NH_3 containing 15 to 18 mg H_2O/liter – over the cooled (room-temperature) powder.[13] Stabilization can also be achieved by

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[12] J. S. Anderson et al., The Properties and Microstructure of Uranium Dioxide; Their Dependence upon the Mode of Preparation, AERE-C/R-886 (August 1952).

[13] Y. Carteret, P. Chenebault, and R. Delmas, Canadian Patent No. 646,474 (Aug. 7, 1962).

adding organic liquids, such as alcohol or CCl_4, to a drum containing the unstabilized powder and allowing the vapor to penetrate the powder.[13] We have found that adding 5 g H_2O to approximately 550 g of UO_2 with a surface area of 10 to 13 m^2/g also prevents the ignition of the UO_2 powder when exposed directly to air. It is necessary, however, to tumble the powder so that the moisture is evenly distributed throughout it.

The action of the processes described above must be to inhibit the chemisorption of the oxygen by the UO_2. Presumably, the same sites are used initially by the water or organic material, perhaps with release of energy; but ignition cannot take place without a supply of oxygen. The replacement of the absorbed molecule by oxygen does not produce a great enough temperature rise to cause ignition, either by reason of time or by reason of insufficient difference in the heats of absorption.

Stabilization of UO_2 with Dry Ice

Dry ice (solid CO_2) has been used to stabilize UO_2 when the powder is at an elevated temperature. Finely powdered dry ice can be used to cover the UO_2, providing a gas blanket as well as cooling the material to below room temperature. The volume ratio of dry ice to UO_2 is usually 4 or 5. After the material is at or below room temperature, the dry ice is physically mixed with the UO_2 powder on a flat surface and allowed to stand until all the dry ice has evaporated.

The substantial cooling of the powder causes condensation of atmospheric moisture on the UO_2; moisture determinations after evaporation of the dry ice have revealed as much as 2% in the UO_2 powder. However, the powder will dry on standing to an amount in equilibrium with the atmosphere (something less than 1%, depending on the relative humidity).

The stabilization by this means, which can be used successfully on powders up to 20 m^2/g, may be a combination of protection by moisture, as described above, and the controlled exposure to air by the gradual removal of the CO_2 blanket.

Mechanical Stabilization of UO_2

Uranium dioxide can be prevented from igniting on exposure to air by maintaining the powder below the ignition temperature. The previously described techniques are all means of accomplishing this temperature control. The same effect can be accomplished by exposing so thin a layer of fresh UO_2 to air that the heat of absorption is dissipated to the atmosphere or to a cooling plate, so that the temperature of the UO_2 is not raised above its ignition temperature. Caputo and Perry,[14] for example, describe one such technique for a continuous UO_2 production process. Their powder was held at or slightly above room temperature by removing the heat of reaction with a water-cooled trough and by blowing cooled air over the powder.

We have used a procedure of this same general nature, and the apparatus is shown in Fig. 3. Uranium dioxide powder was transferred from an inert atmosphere through a hopper onto one end of a covered 3 1/2-in.-wide × 3/4-in.-deep × 6-ft-long aluminum tray. Argon gas blanketed the UO_2, both coming out through the hopper and also from a tube that carried it directly to a point in the plastic cover of the tray 6 in. in front of the hopper. The UO_2 powder was moved from under the hopper and down the tray by the action of a Syntron vibrator; the gap between the end of the hopper tube and the tray was about 3/32 in. At the midpoint of the 6-ft-long tray the powder met a counter current flow of air, coming from the exit end of the tray. Both the argon and air were bubbled through water before being admitted to the tray; both gases exited up a tube leading from the center of the tray's cover.

The light-brown UO_2 powder could be seen through the plastic top to darken as it passed the midpoint of the vibrating tray. The restriction between the bottom of the 2 1/2-in.-diam hopper discharge end and the bottom of the tray (3/32 in.) ensured that the powder moving down the tray was sufficiently shallow that the heat of absorption did not raise the temperature of the powder to the ignition point, even when powders of 13 m^2/g surface area were being stabilized.

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[14] A. J. Caputo and J. E. Perry, Production, Precision Forming and Sintering of Ceramic-Grade UO_2, Y-1301 (1961).

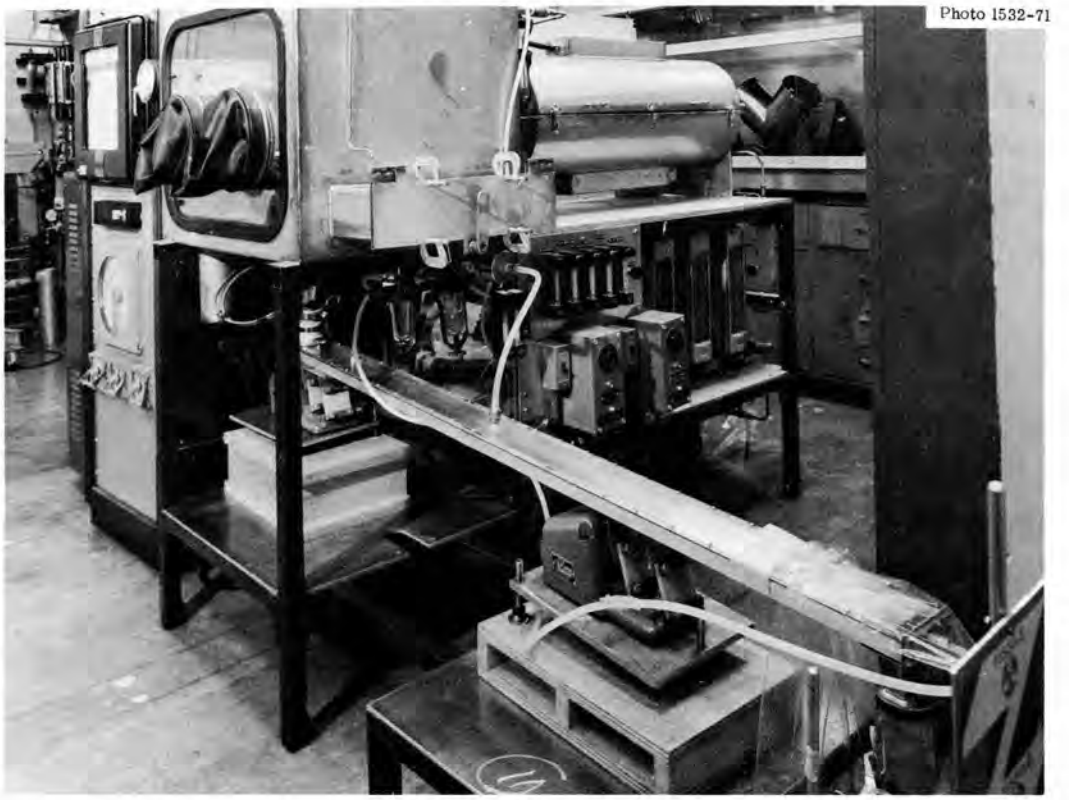

Fig. 3. Reduction and Stabilization Apparatus.

The powder discharged through a slot near the exit end into a removable glass bottle. The glass bottle permitted visual observation of the stabilized powder's behavior.

No attempt was made to optimize this particular design, except to ensure that UO_2 powders with surface areas up to at least 13 m^2/g could be adequately stabilized.

REDUCTION OF URANATE TO UO_2

General Process Description

Because of the relatively small batch size of our process, the chosen procedure was to reduce ammonium uranate (or "yellow cake") by beginning the heating in an argon-filled furnace, changing to hydrogen at the desired temperature, and continuing the process until the desired reduction to UO_2 was completed. Batches were then furnace-cooled in

hydrogen, removed into an argon-filled glove box, stabilized, and sampled as desired.

The work described in the previous section on Stabilization made clear the importance of surface area of the final UO_2 powder for preventing ignition and controlling further pickup of oxygen and moisture. Therefore, to arrive most easily at a powder with a desired surface area, less than about 8 m^2/g, it seemed advisable to perform some preliminary studies in both argon and hydrogen to determine in general the effect of heating at various temperatures on the surface area of the resulting powder. We report on these experiments first and then describe the actual furnace and the results obtained with various procedures.

Effects of Heating Uranate Cake in Argon at Various Temperatures

Surface areas, total uranium, and in some cases NH_3 and NO_3^- contents were measured on samples heated for various times and temperatures in a tube furnace, blanketed with flowing argon. We suspended 2-g samples in platinum buckets in the cold zone of the furnace tube until the desired furnace temperature had been reached. The samples were then raised into the hot zone of the furnace within about 0.5 min and heated for the desired length of time. Samples were cooled by lowering back into the cold zone.

Temperatures were automatically controlled within 20°C; a check of the temperature of the hot zone of the furnace with a standard Pt vs Pt–10% Rh thermocouple revealed no more than 10°C difference from the temperature read on the control unit. The samples heated were from a large powder batch made by dissolving depleted U_3O_8 in HNO_3, precipitating with NH_3 gas to a pH of 8, centrifuging, drying in a microwave oven, and sieving through a 100-mesh screen. Analysis of the starting material revealed 70.27% U, of which less than 0.2 wt % was in the +4 oxidation state; 5.9 wt % NO_3^-; 3.08 wt % NH_3; and, by difference, 6.63 wt % H_2O. Results of the heatings are shown in Table 1.

Table 1. Results[a] from Heating in Argon

Sample	Temperature (°C)	Time of Heating (hr)	NH_3 (wt %)	NO_3^- (wt %)	U (wt %)	Surface Area (m^2/g)
A-4701-111	200	24			79.6	3.43
A-4701-113	300	3	0.12	0.10	80.3	3.02
A-4701-115	300	16			80.7	3.24
A-4701-118	400	1			81.5	5.23
A-4701-116	400	18	0.01	< 0.01	82.4	6.66
A-4701-131	450	2			81.9	7.83
A-4701-130	500	2			83.4	17.4
A-4701-133	300 initially; 500 final	2 2			83.6	18.1
A-4701-120	to 450[b]	48	0.03	< 0.01	82.9	13.2

[a]Starting material was taken from the same "standard" sample of uranate. Samples, about 2 g, were transferred into a hot furnace under argon and then cooled by being lowered out of the hot zone. Sample numbers refer to ORNL notebook page numbers.

[b]This ~ 75-g sample was heated slowly over a period of two days. The sample was above 400°C for about 6 hr and at 450°C for about 1.5 hr before the power was cut. The sample was furnace cooled overnight.

The results reveal some interesting relationships. The general behavior is that the higher temperatures and longer times cause an increase in surface area. Thus, increasing the temperature from 300 to 400°C approximately doubles the surface area (compare samples 115 and 116), and increasing the time from 1 to 18 hr at 400°C increases the surface area about 20%. The reason for the increase in surface area of the resulting powder up to about 450°C appears to be the loss of NH_3, H_2O, and NO_3^- (NO_3^- appears to be present largely as NH_4NO_3) and consequent breaking up of crystals. When wt % U is converted to wt % UO_3, it is seen that for samples heated at and below 450°C the material balance does not equal 100%; we presume this difference is due to sorbed water, for which we did not analyze.

At 500°C the surface area increased dramatically over those of samples heated at lower temperatures. The increase in uranium content to

above that for UO_3 indicates that oxygen is being lost and a more destructive decrepitation takes place in the powder particles. The structures of the uranates[15] appear to be closely related among themselves as well as to that of UO_3. The structures appear to consist of hexagonal layers of the uranium oxide with additional ligand molecules of water and ammonia between the layers. One might infer, therefore, that the loss of water and NH_3 does not break up the crystal as much as the loss of oxygen from the UO_3, which leads to formation of an orthorhombic U_3O_8. Previous studies of calcination of ammonium uranates appear to have been done in air and thus are not directly comparable with this work because of the effect of oxygen on NH_3 and possibly NO_3^-.

Effects of Heating Pretreated Uranate in Hydrogen

Surface areas and total uranium contents were measured on samples of an argon-calcined uranate material (sample 120 in Table 1), which were heated in hydrogen at various temperatures. The procedure was essentially the same as that used to treat uranate cake in argon. Results for the various treatments are presented in Table 2.

The surface areas of the samples heated in hydrogen show a marked decrease with increasing temperature (compare the first three samples of Table 2). There is also an effect on the final surface area by the surface area of the starting material as follows: By referring to Table 1, one can deduce that the sample heated at 300°C in argon (sample 134, Table 2) had a much smaller surface area than the sample heated at 500°C in argon (135, Table 2). After reduction in hydrogen, sample 134 had a smaller surface area than sample 135.

The rationale for the large increase in surface area of the powder heated at 500°C in argon (Table 1) over those heated at lower temperatures was that the crystal structure was drastically changed by the treatment. Comparison of samples heated at 500°C in argon with that heated at 500°C in hydrogen reveals a much smaller surface from the

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[15] J. L. Woolfrey, The Preparation and Calcination of Ammonium Uranates – A Literature Survey, AAEC/TM-476 (September 1968).

Table 2. Results of Heating Pretreated Uranate in Hydrogen

Sample	Pre-treatment	Temperature (°C)	Time[a] (hr)	U (wt %)	Surface Area (m^2/g)
A-4701-122	b	400	2.5	86.1	20.2
A-4701-124	b	500	1.25	86.6	10.7
A-4701-126	b	600	1.7	87.8	6.96
A-4701-134	c	300 in argon; then 500	2 2	87.3	9.2
A-4701-135	c	500 in argon; then 500	2 2	87.5	11.5
A-4701-143	d	500	~ 17	86.8	13.4

[a]Samples were transferred rapidly into a hot furnace and cooled by lowering to the cold zone.

[b]Starting materials were taken from a single batch of uranate heated up to 460°C in argon (sample 120, Table 1).

[c]Material was untreated uranate and was first heated in argon, as described for Table 1, then cooled and hydrogen admitted to the system and the sample raised, heated, and cooled.

[d]A mixture of argon and 4% H_2 was admitted slowly after the sample had first been brought into the hot zone in argon.

hydrogen treatment than might be anticipated. The sample heated at 400°C in hydrogen agrees more with the postulate of a drastic crystal structure change causing the decrepitation. Since the reaction

$$UO_3(s) + H_2(g) \rightarrow UO_2(s) + H_2O(g) \qquad (4)$$

is exothermic to the extent of nearly 23 kcal/mole of UO_3 one might suppose that increased heating of the sample led to some sintering of the powder particles. Sample 143 was run in an attempt to test this hypothesis. The diluting effect of the argon and the slow admission of the Ar–4% H_2 should have allowed the dissipation of much of the heat during reduction. However, the surface area increase might well be accounted for by the increase of surface area of the precursor powder. Thus, there appears to be a sintering effect during the reduction in hydrogen, but more experiments would be necessary to explain it.

Production Reduction Furnace

The brief experiments described above were sufficient to explain reasonably well the results obtained from treatment in the furnace used for all the UO_2 production. As was shown above, the UO_2 obtained depends, in part, on the kind of material used as its precursor. Thus, the data presented in this section are indicative only as results are compared within this set.

The furnace used was an Inconel tube 4 3/4 in. diam × 54 in. long. The center was covered with a 37-in.-long clamshell heater capable of operation up to at least 900°C; this heater can be seen at the upper right of Fig. 3. The heater could be opened to hasten cooling of the furnace after a run. One end of the furnace tube opened into an argon-filled glove box (Fig. 4, right side); the other end had only a port for the hot spent gases to escape through a bubbler. Either argon or hydrogen flowed into the glove-box end of the tube through a preheater. The flow rate was controlled by means of calibrated flowmeters, which can be seen on a panel under the furnace in Fig. 3. A water trap collected most of the moisture released from the reduction. Unreacted hydrogen was burned before being released. The temperature cycle of the furnace was controlled by means of an L and N Trendtrak control unit, sensing temperature from a thermocouple placed on the outside center of the furnace tube. Thus, a lag existed between the control setting of the furnace and the sample. A thermocouple placed in a well over the center of the boats could be used to estimate the extent of the temperature lag. At the high heating rates (greater than 200°C/hr) as much as 40°C lag was observed. About 20 min was required to bring the inside temperature within less than 10° of the outside set point after a constant outside temperature was established on the furnace tube.

Two Inconel boats were used to contain the dried uranate in the furnace. These were placed symmetrically, one behind the other, in the furnace tube on runners welded to the inside of the tube. Thus, the temperature measurement at the center of the furnace referred always to one end of each boat. A temperature gradient existed along the furnace tube: When the inside center was at 600°C, the temperature in the inside

Fig. 4. Glove Box and Controller Panel for Process Furnace.

tube at the end of the rear boat was 445°C. This temperature gradient resulted in a gradient in the surface area of the powder.

Because of the temperature gradient along the furnace, the surface areas of the powder in the front of the furnace (at one end of the last boat put into the furnace) would be expected to be different than the surface area of the powder in the center of the furnace (at the other end of last boat). This expectation was borne out, as will be seen. The surface area of a blended batch of powder, then, would be expected to be near the average of the two results, which was demonstrated by experiment. Because the amount of oxygen and moisture sorbed by the powder is a function of surface area, one also expects the values for these results to depend on where the sample was taken from the furnace charge. In general, samples for chemical analyses from production runs were taken from stabilized material that had been blended, but samples from developmental runs were taken from the furnace center.

Several surface area measurements on samples run in the process furnace under varying conditions are reported in Table 3. The cams used to program the heating cycles are described in Table 4.

Table 3 shows that heating to higher temperatures in the process furnace before admitting the hydrogen results in a lower surface area of the final UO_2 powder. (This observation agrees with the experiments reported in Table 2.) For example, compare runs in which cam 6 was used with runs in which lower numbered cams were used with the same preflow of argon. Another comparison of the same type is that of runs 55 and 68 in which the same cam, No. 6, was used but the argon preflow was different. Run 55 produced a surface area of 10.2, but 68 with longer argon preflow gave a surface area of 6.0 m^2/g. There is some variation in the surface areas even when the conditions were supposedly the same. We believe the variation in the hydrogen flow rate is probably great enough to cause these differences (compare run 53 with 69). Runs 85 and 87 were used to determine the effect of a drastic variation in flow rate and a large change in argon preflow time, respectively. The effect of increased argon preflow time (run 87) was much as expected; the average surface area dropped considerably. Note that the front is quite different from the back, representing both the effect of some lag in the front

Table 3. Effects on Heat Rate and Gas Flow on UO_2 Surface Area[a]

Sample	Cam[b]	Time of Argon Flow (hr)	Surface Area,[c] m^2/g		
			Average	Front	Back
BD-Lot 1	1	2	13.0–20.0		
BD-Lot 2	1	2	13.0		
BD-Lot 3	1	2	20.0		
A5331-48	2A	0	20.7		
A5331-49	2A	2	16.6		
A5331-50	2	2	13.2		
A5331-52	4	2	15.2		
A5331-53	3	2	12.7		
A5331-55	6	2.5	10.2		
A5331-56	6	2	10.9		
A5331-68 CS Lot 1	6	3	6.01		
A5331-69 CS Lot 2	3	2	11.3		
BD-Lot 4	6	3	6.35		
BD-Lot 5	6	3	7.46		
A5331-85[d] CS Lot 3	6	2.3	11.5	7.8	13.9
A5331-87 CS Lot 4	6	4.0	4.0	9.9	2.3

[a]All samples (500 g U each) were precipitated from 0.4 N HNO_3, 100 g U/liter with gaseous NH_3 in a recirculating system, centrifuged, dried in a microwave oven, and reduced as described above. Gas flow entered at dry box end of furnace tube and exited through a bubbler at the other end. After these measurements, a diffuser tube was added. Flow rates were 0.4 liter/sec except for hydrogen on sample 85.

[b]See Table 4 for description of heating cycle corresponding to cam number.

[c]Surface areas were measured by the BET method by Analytical Chemistry.

[d]Hydrogen flow rate 2.0 liter/sec.

and, probably, some effect of micro-sintering in the back. The fast flow gave a quite different result. Note the reversed effect of position on surface area. This reversal was verified in a separate experiment, which gave almost identical results. We attribute the low surface area in front to a heating of the powder by the rapidly flowing hydrogen.

Table 4. Description of Program Heating Cams

Cam	Heating Cycle
1	Room temperature to 200°C at 100°C/hr; 200 to 300°C at 50°C/hr; 300 to 350°C at 100°C/hr; 350 to 400°C at 30°C/hr; 440 to 700°C at 100°C/hr; Hold at 700°C for 2 hr, furnace cool.
2A	Same as cam 1, except upper temperature is 750°C.
2	Same as cam 1, expect upper temperature is 850°C.
3	Room temperature to 850°C at 120°C/hr; Hold 5 1/2 hr; furnace cool.
4	Room temperature to 700°C at 100°C/hr; Hold 2 hr; furnace cool.
6	Room temperature to 850°C at 200°C/hr; Hold 5 hr 40 min; furnace cool.
9	Room temperature to 680°C at 200°C/hr; Hold 5 hr 30 min; furnace cool.
10	Room temperature to 600°C at 200°C/hr; Hold 5 hr 30 min; furnace cool.

The powder in the rear of the furnace was reduced more slowly because of depletion of the hydrogen from the flowing stream. (It would be well to note that 47 liters of hydrogen would be required if all of the gas were used for reduction from UO_3 to UO_2. With the slow flow rate a minimum of 120 min is required, but for the fast flow only 24 min.)

DRYING OF AMMONIUM URANATE

After precipitation of ammonium uranate from a uranyl nitrate solution, the precipitate must be separated from the solution and dried before reduction. We have centrifuged the wet slurry, as shown in Fig. 5, decanted the supernate, and dried the moist "yellow cake" in a microwave oven shown in Fig. 6. The centrifuging step was always constant at 600g for 2 min. The decanting step was also constant. However, we varied the conditions of the microwave drying to determine possible effects on both the uranate and the final UO_2 powder. In this section

Fig. 5. Centrifuge Used for Separating Uranate from Another Liquor.

we report experiments investigating the effects of drying conditions on both intermediate and final product.

Three variables were investigated: the time of drying, the temperature of drying, and the effect of crushing. The ammonium uranate was analyzed for NH_3, H_2O, NO_3^-, total U, and BET surface area. On the reduced oxide we measured the tap density and the surface area. The precipitation and subsequent reduction steps were kept as nearly constant as possible. Samples of the final oxide were taken from the center of the furnace rather than from a blended average product; thus they corresponded to a fixed reduction temperature of 600°C rather than an average. The microwave oven was purchased from the Reeve Manufacturing Company. Inside the oven we installed a rotating platform on which the Teflon tubes in which the uranate was centrifuged could sit in a circle. In this way, the tubes containing the uranate all experienced the same power by rotating through the microwave field. A blower was installed to move the moist air out of the tubes during drying.

Photo 1534-71

Fig. 6. Microwave Oven Used to Dry Uranate Samples. A sample is being removed from the rotating table.

Eight runs were made to determine the effects of drying time, microwave power level (drying temperature), and grinding on the ammonium uranate and the final UO_2 powder. The conditions and results of these runs are shown in Table 5.

Grinding did not affect the surface area of the final UO_2 powder; furthermore, we do not believe that it affects any of the other properties. As expected, the H_2O/U mole ratio was decreased both by increased temperature and by increased time in the oven. The NH_3/U mole ratio also decreased but not nearly so dramatically, indicating that water was being selectively removed. The NO_3^-/U mole ratio remained constant for all the cases, indicating no effect by change of the drying parameters.

The surface area of the uranate cake was decreased both as the temperature was increased and as the heating time was increased, although

Table 5. Effects of Drying Cycle Parameters on Ammonium Uranate and UO_2

Run	Temperature (°C)	Time (min)	Ground	Ammonium Uranate								Reduced Oxide[c]	
				NH_3 (wt %)	H_2O[a] (wt %)	U (wt %)	NO_3^- (wt %)	NH_3/U Mole Ratio	Surface Area[b] Case 1 (m^2/g)	Surface Area[b] Case 2 (m^2/g)	Surface Area[b] Case 2 (m^2/g of U)	Tap Density (g/cm^3)	Surface Area (m^2/g)
90A	78[d]	45	Yes	3.22	18.9	60.5	5.2	0.741	7.87	8.60	14.2	1.91	5.69
90B	78	45	No									1.84	5.74
92A	78	80	Yes	3.21	10.7	66.9	5.7	0.672	5.25	7.06	10.6	1.89	5.94
92B	78	80	No									1.90	5.98
91A	115[e]	45[f]	Yes	3.18	5.8	70.7		0.630	5.23	5.58	10.0	1.79	5.42
91B	115[e]	45[f]	No									1.80	5.51
93A	115[e]	80[g]	Yes	3.16	2.7	73.4	6.2	0.603	4.10	5.12	7.1	1.78	6.69
93B	115[e]	80[g]	No									1.89	6.70

[a] Wt % H_2O calculated by subtracting wt % U (as UO_3), NO_3^- (as HNO_3), and bound NH_3 from 100%.

[b] Case 1 is a sample that was degassed 30 min in vacuum at 120°C. Case 2 is a sample that was degassed 50 min in vacuum at 60°C.

[c] Precipitation cycle: 100 g U/liter, 0.4 M HNO_3 at ambient temperature (rising to 42°C) to pH 8.0; no digestion. Reduction cycle: 500 g U to 600°C at 200°C/hr; hold 5 hr and cool. First 3 1/2 hr in argon at 0.4 liter/min, then H_2 at 0.4 liter/min. Samples were taken from the center of the furnace, corresponding to 600°C.

[d] Temperature during most of the cycle corresponds to 0.2-A setting on microwave oven.

[e] Preheat for 15 min at 0.2 A; then increase setting to 0.4 A. Temperature reached after 45 min.

[f] Weekend delay between preheated cycle and high power cycle.

[g] Temperature of uranate cake dropped to 108°C during the long high-power cycle, probably due to the inability of the cake to absorb energy after the moisture content reached some critical value.

the temperature effect was more pronounced. This appears to indicate a growth of the crystallites during drying. (The measurement is somewhat ambiguous because of the effect on the results of outgassing of the sample during the initial step of the BET measurement, as shown by comparison of the surface areas for cases 1 and 2 in Table 5.)

Increasing either temperature or time of drying appears to result in an increased surface area of the final powder but a decrease in surface of uranate. Even though the effect on the final powder is not large, it is significant in that it runs counter to the statement by Woolfrey[16] that the surface area of UO_2 powders depends on the surface area of the materials from which they are prepared. It seems clear that a more complicated process is involved in determining the final UO_2 surface area. Since elucidation of such mechanisms was not the purpose of this investigation, no further work was done on this matter. The basic conclusion was that drying conditions had little discernible effect on the final UO_2 product.

DISSOLUTION

The feed material for the $^{233}UO_2$ production line will be purified uranyl nitrate solution from an ion-exchange purification system. The free nitric acid content will be approximately 0.1 N. For this study, because of the ready availability of high-quality enriched U_3O_8, dissolution of the oxide in nitric acid to obtain the uranyl nitrate solution was the chosen means for production of this starting material.

Dissolution of the U_3O_8 was assumed to take place via the reaction:

$$U_3O_8 + 8HNO_3 \rightarrow 3UO_2(NO_3)_2 + 2NO_2 + 4H_2O \ .$$

In point of fact, there might as well be expected some of the reaction

$$3U_3O_8 + 20HNO_3 \rightarrow 9UO_2(NO_3)_2 + 2NO + 10H_2O \ ,$$

[16] J. L. Woolfrey, The Preparation and Calcination of Ammonium Uranates – A Literature Survey, AAEC/TM-476 (September 1968).

and the actual reaction is undoubtedly some combination of the two. The uncertainty in the HNO_3 concentration of the resulting solution calculated from the first equation and the quantities of materials used is less than 0.1 N and is probably about 0.05 N.

The oxide was dissolved by adding the required amount of concentrated acid to an equal volume of water and pouring the mixture directly on the powdered U_3O_8. The reaction took place in a heavy wall glass pipe, 4 in. diam × 18 in. high. The U_3O_8 was of such a particle size that stirring was necessary toward the end of the reaction. The reaction pipe can be seen in the center of Fig. 7.

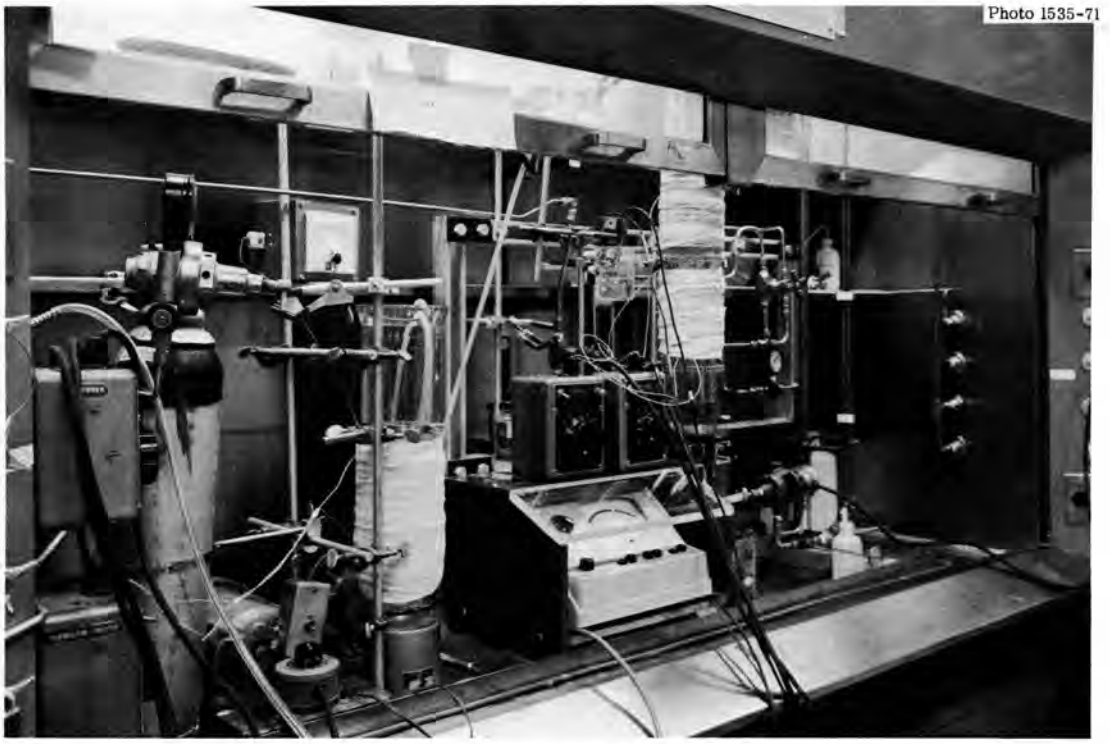

Fig. 7. View of Dissolution and Precipitating Equipment from Left Side.

After the dissolution was complete, enough water was added to the solution to make approximately 2 liters. Usually the solution was allowed to stand overnight before pumping into the precipitation vessel. Dilution prevented uranyl nitrate from crystallizing in either the dissolver or in the line between the dissolver and the precipitator.

PRECIPITATION OF AMMONIUM URANATE

Many, if not most, of the possible variations in the precipitation procedure will affect the properties of the resulting ammonium uranate, according to the review by Woolfrey.[16] The purpose of this study, rather than to gain a mechanistic understanding of the process, was to define the effects of moderate variations in the various production parameters on the uranate cake and final UO_2 product as a guide to ease and reproducibility of production. Consequently, four parameters were investigated: the temperature of precipitation, the final pH of precipitation, the initial HNO_3 concentration, and the time of digestion after precipitation was complete.

Woolfrey[16] has reviewed the voluminous literature on the subject up to 1968 and noted the conflicting results that have been reported. Stuart and Whateley[17] note that there is adequate proof in the literature that ammonium diuranate, $(NH_4)_2U_2O_7$, can never be prepared in aqueous solution, even in the presence of a large excess of ammonia. Thus, even the commonly used term ADU (for ammonium diuranate) is actually a misnomer.

There is, however, considerable uncertainty even yet about the various compounds in the UO_3-NH_3-H_2O system. The careful work by Cordfunke[18] seemed to establish four distinct compounds by x-ray diffraction and chemical analysis. More recently, Stuart and Whateley[17] have indicated that the stretching frequency of the uranyl ion varies continuously with NH_3/U mole ratio rather than discontinuously. They reasonably interpret these results as indicating that the NH_3/U ratio varies continuously rather than exhibiting fixed values as indicated by Cordfunke.[18] However, Stuart and Whateley's results apply to fully hydrated samples, equilibrated at room temperature, while Cordfunke's studies were on samples equilibrated at 40°C. The difference in temperature may explain the difference in results. In any case, these results

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[17]W. I. Stuart and T. L. Whateley, "Composition and Structure of Ammonium Uranates," J. Inorg. Nucl. Chem. 31, 1639–1647 (1969).

[18]E.H.P. Cordfunke, "On the Uranates of Ammonium – I. The Ternary System NH_3-UO_3-H_2O," J. Inorg. Nucl. Chem. 24, 303–307 (1962).

are cited to indicate the difficulty in assigning definite compositions to compounds in the system. The slow rate of attaining equilibrium is also very likely responsible for some of the variation in results reported in the literature.

Process Description

Our precipitation was carried out as a batch process in a recirculating system. A stainless steel pump circulated the solution and slurry from the bottom of a heavy-walled glass pipe through a stainless steel tube to the top of the pipe throughout the operation at the rate of 27 liters/min. Ammonia gas was injected through a flowmeter into the inlet to the pump at a rate of 0.25 moles/min. In each case 500 g U (as uranate) was precipitated so that approximately 16 min was required to precipitate the uranate after the free acid was neutralized.

The glass pipe used as the vessel was designed to be critically safe. It was 4 in. ID and covered with a heating tape to preheat the solution. The tube through which the solution was pumped on the way to the top of the vessel was water jacketed, and a constant low temperature could be maintained by suitably adjusting the flow of cooling water through it. The temperature of the solution was monitored at a point near where the NH_3 was injected. On occasion the temperature at the top of the solution was also monitored, and the difference was less than 3°C. Figures 7 and 8 show two views of the apparatus.

After the precipitation was complete, as indicated by the desired pH, the precipitate was centrifuged from the remaining solution. It is probably important to note that the precipitate was not washed and that the supernate was decanted from the precipitate. In attempting to correlate our results with other work in the literature, this point is undoubtedly relevant. During washing, some hydrolysis and nitrate removal undoubtedly takes place. Further, since we will show some effect of nitrate concentration on the final product, the lack of washing must influence the results.

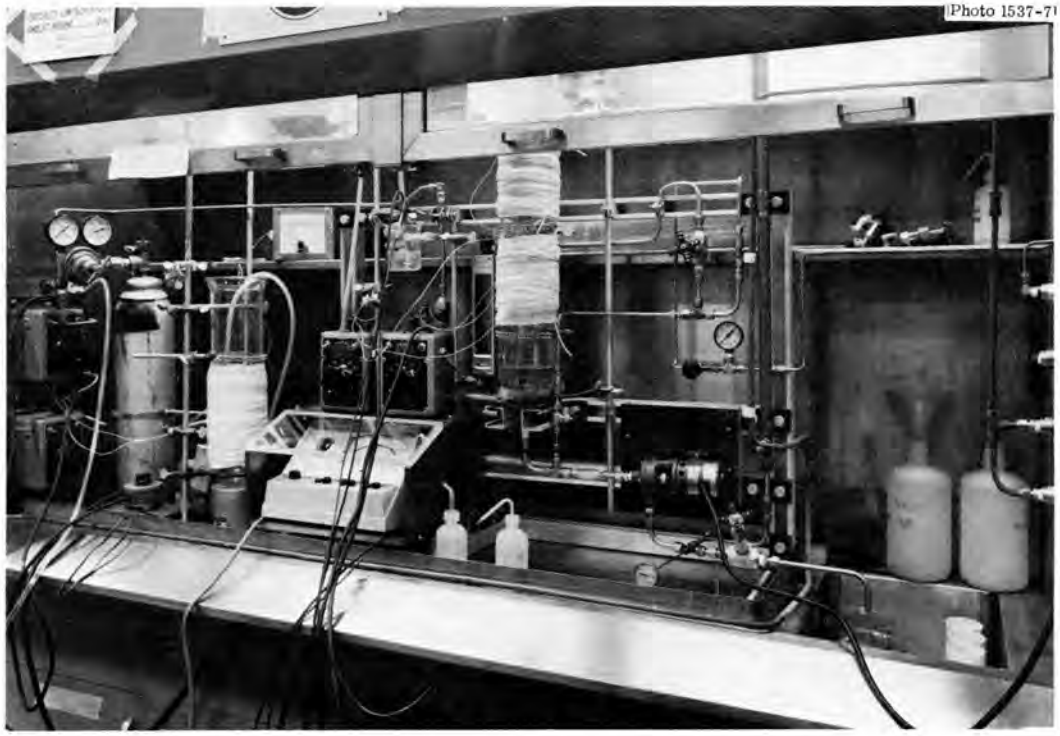


Fig. 8. View of Precipitation Apparatus from Right of Hood.

Effects of Varying Precipitation Parameters

We made 16 runs in a factorial experiment to investigate the effects of precipitation variables on both the ammonium uranate and the UO_2 powder. The temperature of precipitation was varied from a low of 22 to 30°C to a high of 54 to 62°C. The pH was varied from a low of 5 to 6 to a high of 8.7 to 9.2. The HNO_3 concentration was varied from a low of 0.4 M to a high of 1.4 M. The time of digestion after precipitation was complete was varied from a low of 0 to 10 min to a high of 120 min. Results are shown in Table 6.

The results can be paired to determine the effect of any of the four precipitation conditions on any of the six measured quantities. For example, runs 97A and 97B were the same except for the variation in the digestion time. A measure of the effect of digestion time on, say, surface area can be obtained by subtracting the value of the surface area in run 97A from that in run 97B. The general effect of digestion time on surface area can be obtained by averaging the surface area

Table 6. Effects of Precipitation Variables on Ammonium Uranate and UO_2 Powder

Run		Precipitation Conditions				Analysis of Uranate Cake[a]						UO_2 Powder[b]	
		Temperature (°C)	pH	HNO_3 (M)	Time (min)	H_2O (wt %)	NH_3 (wt %)	Total U (wt %)	NO_3 (wt %)	NH_3/U Mole Ratio	NO_3/U Mole Ratio	Surface Area (m^2/g)	Tap Density (g/cm^3)
A5331-116-1	97A	22–30	5–6	0.4	0–10	14.3	3.38	62.1	7.69	0.761	0.475	7.88	2.22
-116-2	97B	22–30	5–6	0.4	120	5.3	3.50	69.2	8.05	0.708	0.447	8.49	2.25
-116-3	98A	22–30	8.7–9.2	0.4	0–10	14.1	3.94	62.2	7.17	0.887	0.443	8.00	1.27
-116-4	98B	22–30	8.7–9.2	0.4	120	17.8	3.73	65.3	6.10	0.740	0.252	8.25	1.23
A5331-117-1	99A	22–30	5–6	1.4	0–10	14.4	4.05	59.4	10.20	0.955	0.659	7.47	1.86
	99B	22–30	5–6	1.4	120	5.35[c]	4.17[c]	66.5[c]	10.56[c]			8.08[c]	1.89[c]
-117-2	100A	22–30	8.7–9.2	1.4	0–10	36.1	3.54	44.0	7.44	1.130	0.649	7.56	1.25
-117-3	100B	22–30	8.7–9.2	1.4	120	31.9	3.81	47.8	6.80	1.120	0.546	6.05	1.07
-117-4	101A	54–62	5–6	0.4	0–10	12.7	2.76	66.5	4.62	0.581	0.267	6.24	1.87
A5331-118-1	101B	54–62	5–6	0.4	120	10.0	2.98	68.6	4.57	0.608	0.256	7.25	1.58
-118-2	102A	54–62	8.7–9.2	0.4	0–10	12.3	3.03	66.4	4.87	0.639	0.281	7.20	1.51
-118-3	102B	54–62	8.7–9.2	0.4	45[d]	7.1	2.95	71.8	3.68	0.575	0.197	5.82	1.59
-118-4	103A	54–62	8.7–9.2	1.4	0–10	21.5	3.39	57.9	5.58	0.820	0.370	6.07	1.61
A5331-120-1	103B	54–62	8.7–9.2	1.4	120	8.0	3.30	69.4	5.29	0.666	0.292	9.82	1.46
-120-2	104A	54–62	5–6	1.4	0–10	11.4	3.02	65.6	6.76	0.644	0.395	10.4	1.76
-120-3	104B	54–62	5–6	1.4	120	12.1	2.97	65.7	6.00	0.632	0.350	9.57	1.93

[a]Drying cycle: 0.2 A for 15 min.; 0.3 A for 45 min. (microwave oven); H_2O obtained by difference.

[b]Reduction cycle was room temperature to 600°C at 200°C/hr, hold 5.5 hr, furnace cool. First 3 1/2 hr in Ar at 0.4 liter/min; the remainder of the time in H_2 at 0.4 liter/min. Samples were all taken from the portion in the center of the furnace where the thermocouple was, so that the data apply to material reduced at 600°C and do not constitute an average as do results from production samples.

[c]Estimation based on other runs.

[d]Time reduced due to leak in recirculating pump.

difference from all eight pairs. A simple way to do this averaging mathematically is to treat the measured result (in this case, surface area) from the low end of the range of the controlled parameter (in this case, digestion time) as negative in sign and that from the high end as positive. Then add all results together algebraically and divide by the number of pairs, eight in this case. One would thus obtain from Table 6: $(-7.88 + 8.49 - 8.00 + 8.25 - 7.47 + 8.08 - 7.56 + 6.05 - 6.24 + 7.25 - 7.20 + 5.82 - 6.07 + 9.82 - 10.4 + 9.57)/8 = + 2.51/8 = 0.31$ m^2/g. Cross effects (for example, the effect of increasing both the precipitation temperature and the HNO_3 concentration on the surface area) can likewise be determined from these results. A subtraction process such as described above can be used. Alternatively and easier one can assign signs to the conditions (precipitation temperature and HNO_3 concentration, for example) and multiply the signs algebraically. The resulting sign product is assigned to the measured result; the values are added algebraically, and the result is divided by the number of pairs.

A review of the data in Table 6 shows that the surface area of the UO_2 powder can be varied from 5.8 to 10.4 m^2/g by varying the temperature of precipitation, the final pH of the slurry containing the precipitate, the HNO_3 content of the starting material, and the digestion time. (Note that this surface area change is approximately the same as that from changing the reduction temperature from 500 to 600°C.) The biggest single effect is a surface area decrease of 0.83 m^2/g from changing the final pH. Almost as important was the effect of the initial HNO_3 content: An increase from 0.4 to 1.4 M resulted in an increase of 0.74 m^2/g in the final UO_2 surface area. An increase in digestion time from 0–10 to 120 min resulted in an increase of 0.313 m^2/g, while the changing precipitation temperature apparently had almost no effect: an increase of only 0.07 m^2/g.

The cross effects in the system are quite interesting: for example, the effect of high pH and high HNO_3 was to decrease the surface area of the UO_2 by 0.68 m^2/g, while the effect of the combination of high temperature and high HNO_3 was to increase the surface area by 1.60 m^2/g. The results from these cross effect calculations indicate the complexity of the system and explain, to some degree, the conflicting data reported in

the literature. The prediction one might make regarding the effect of a single parameter must be made with care; for example, precipitation to a high pH combined with a high original HNO_3 concentration results in a product having a considerably different surface area from that obtained by using solutions with a low HNO_3 concentration and precipitation to a high pH. In very little of the published literature on precipitation effects are sufficient data given so that meaningful cross comparisons of this type can be made.

As discussed in the Stabilization section of this report, surface area of the UO_2 is important because of the pyrophoricity of high-surface-area powder. Further, the rate of pickup of oxygen and moisture from the atmosphere also depends on the surface area. And, finally, surface area of the powder is to some extent related to the particle size, and this relates to the amount of fines present in the powder. For these reasons we have emphasized the effects of the various treatments on the surface area.

Other considerations are important as well, of course. One of these is the handleability of the powder. Although we do not have a quantitative measurement of handleability, some powders broke up more easily and were more free flowing than others. This information is important from the practical standpoint of moving the powders.

From the standpoints of surface area control and handleability, high pH values at high precipitation temperatures appear to yield the best powders. However, because of the volatility of NH_3, a compromise to somewhat lower pH values and temperatures is probably desirable. However, in the experiments reported here, material made under conditions of low temperature, low pH, long digestion time, and high HNO_3 content would not centrifuge in 8 min at 400g.

The tap density of a powder is another useful quantity, although it is only quantitative in the sense that it can be compared within a given study. Of the individual parameters, only the pH appeared to affect the tap density when the standard factorial treatment was applied, reducing the density by 0.55 g/cm^3 when the final pH was changed from 5–6 to 8.7–9.2. However, the cross effect of temperature with pH reveals a

reduction of 0.30 g/cm^3 in the tap density. This observation indicates there is a temperature effect which is unrevealed by the individual parameter treatment. Thus, by treating the density data from low temperature the effect of pH is a −0.85, while at the high temperature the effect of the experimental pH change (E_{pH}) is only a −0.24. At low temperatures E_{HNO_3} is −0.22, while at high temperatures E_{HNO_3} = +0.05. The combination makes the overall result appear as if no significant effect is seen.

Similar treatments can be made of the effects of the precipitation conditions on the chemical content of the ammonium uranate cake. One sees that the NH_3/U mole ratio is decreased by increasing digestion temperature (−0.254), decreased by increased digestion time (−0.059), increased by increasing pH of precipitation (+0.099), and also increased by addition of HNO_3 (+0.170). The NO_3^-/U mole ratio is decreased by increasing digestion temperature (−0.20), decreased by increasing digestion time (−0.08), decreased by an increasing pH (−0.05), and increased by increasing HNO_3 in the starting solution (+0.15).

Examination of Powder Produced in Precipitation Study by Scanning Electron Microscope

To obtain an indication of the morphology of the powders produced in the precipitation study, a selected number were examined in the scanning electron microscope. The observations are recorded in this section.

A-5331-97A, Uranate Precursor of A-5331-116-1

Two kinds of precipitate are revealed in the uranate precursor by the scanning electron microscope (SEM). Figure 9 shows both types together at 1700×. Figure 10 shows (a) a higher magnification of the smooth crystalline type and (b) a much higher magnification of what appears to be fluffy in Fig. 9 and appears to be present in much higher proportion. The more crystalline particle is reminiscent of particles

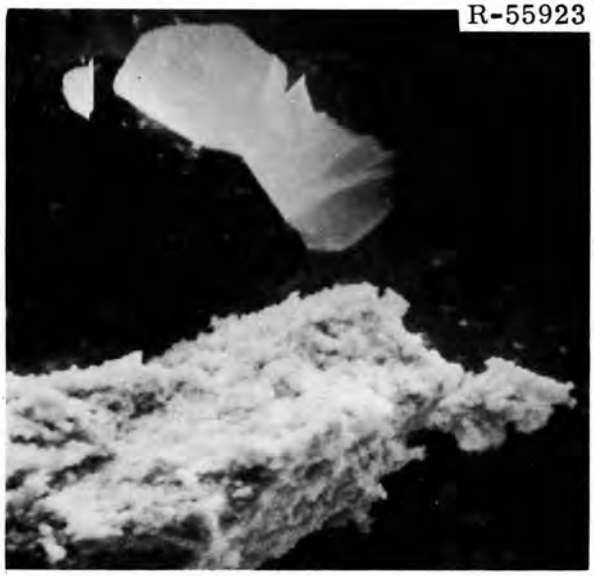
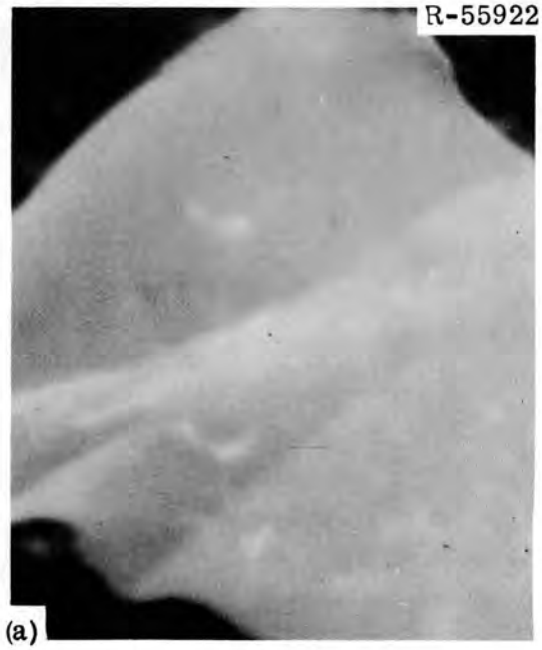


Fig. 9. Sample 5331-97A, Uranate Precursor of A-5331-116-1. 1700×.

of $(NH_4)_4UO_2(CO_3)_3$, which is shown in Fig. 11. Sample 97A contained 0.18% CO_3^{2-} by weight. Another sample (97B), which was identical to it except that it had been digested 2 hr after precipitation was complete, contained 0.34% CO_3^{2-}. Sample 97A possibly had 0.4% of the total uranium present bound as carbonate, assuming it was present as $(NH_4)_4UO_2(CO_3)_3$.



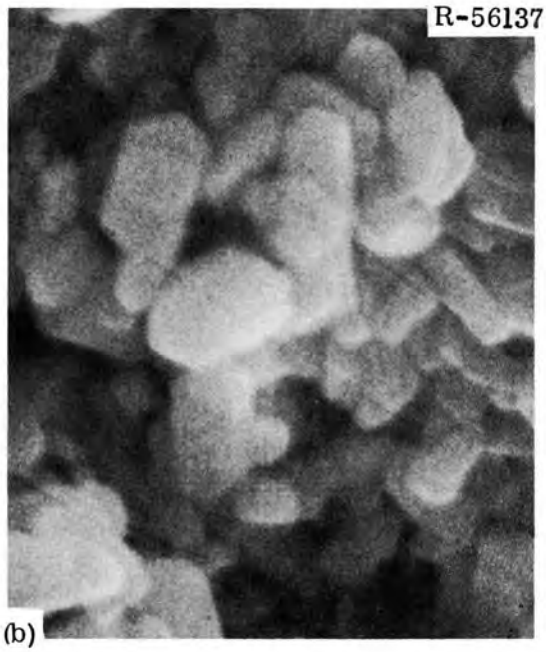


Fig. 10. Sample A-5331-97A. (a) Smooth crystalline portion. 8500×. (b) Fluffy portion. 30,000×.

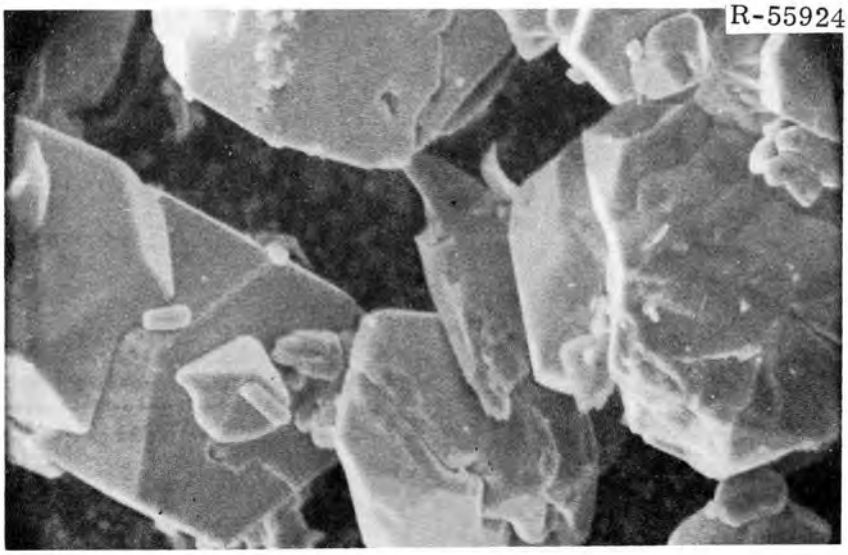


Fig. 11. $(NH_4)_4UO_2(CO_3)_3$. 1200×.

A-5331-116-1 (UO_2)

Examination of the UO_2 appears to indicate that a range of particle sizes occurs in this material. Figure 12 shows what appear to be small particles as well as large, smooth surfaces. We have postulated this kind of occurrence to explain the behavior of material during the stabilization experiments in a previous section.

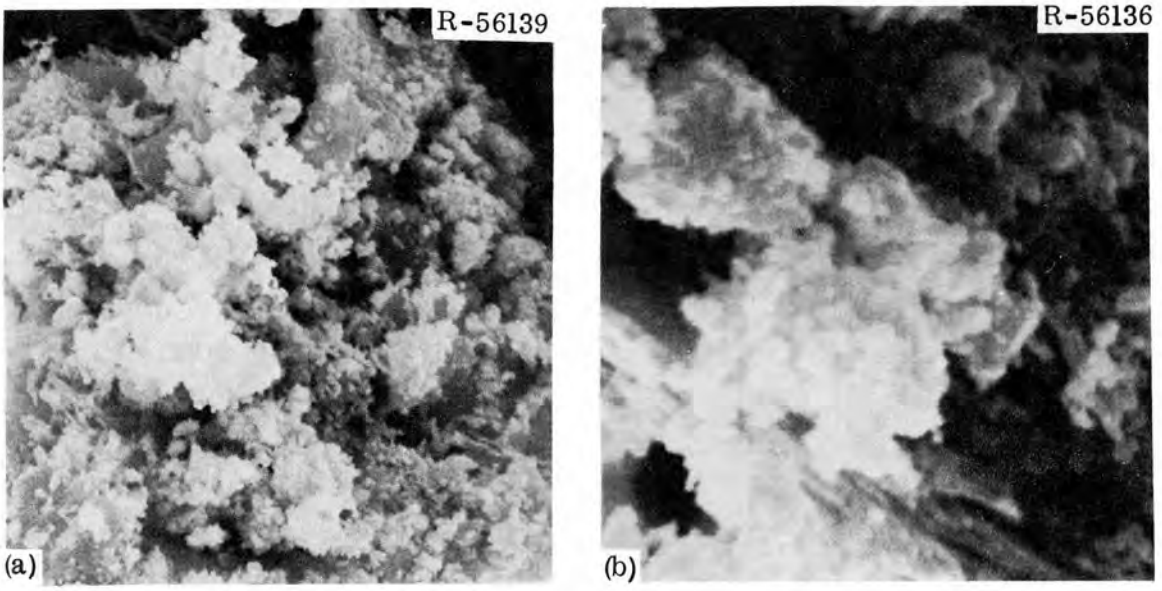


Fig. 12. A-5331-116-1 UO_2. (a) 3000×. (b) 10,000×.

A-5331-116-2 (UO_2)

Only one morphology was seen in the sample examined of this material. Two magnifications are shown in Fig. 13. For some unknown reason, resolution of the individual particles of the UO_2 has proved much more difficult than for other oxides examined – for example, TiO_2. Figure 13(b) represents one of the better attempts. The smaller particles seen at 50,000× are about 1×10^{-5} cm in diameter. The UO_2 powder had a measured surface area of 8.5 m^2/g, which would correspond to 3.3×10^{-6} cm in diameter if spherical particles are assumed and a density of 10.8 g/cm^3 is used in the calculation. A discrepancy of a factor of 3 is thus seen, which implies that either the density is incorrect or the surface is rough.

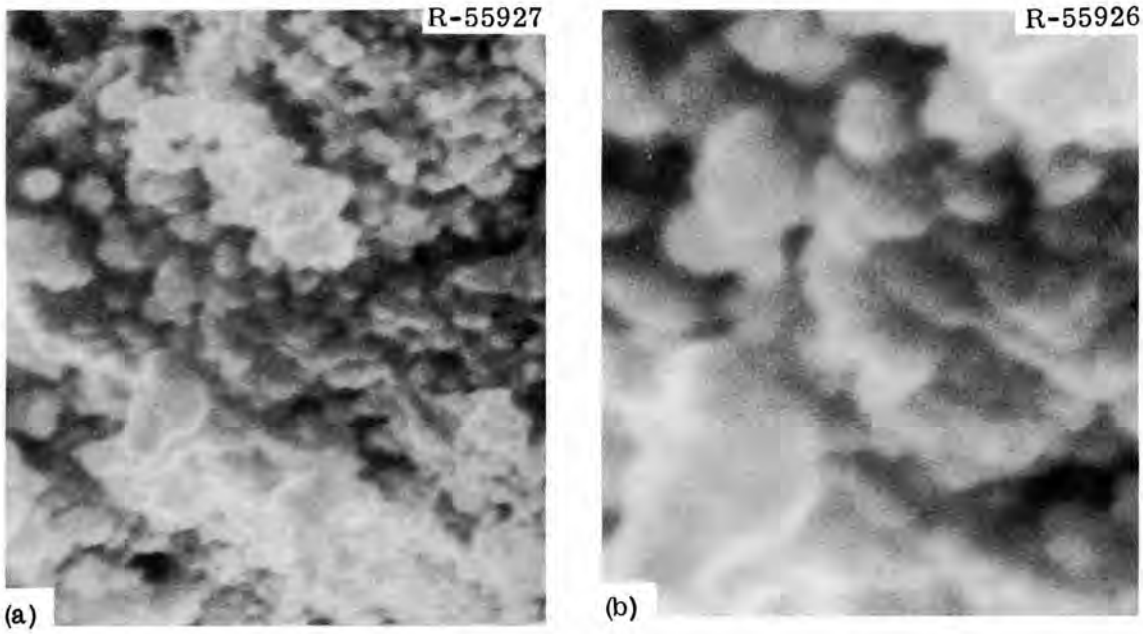


Fig. 13. A-5331-116-2 UO_2. (a) 20,000×. (b) 50,000×.

A-5331-116-3 and A-5331-116-4 (UO_2)

These samples were rather similar in morphology; hence, only A-5331-116-4 is shown. Two different morphologies can be seen in these SEM pictures. Figure 14(a) (7500×) shows both morphologies, a smooth, curled platelet-like material, and "fluffy" material. The "fluffy"

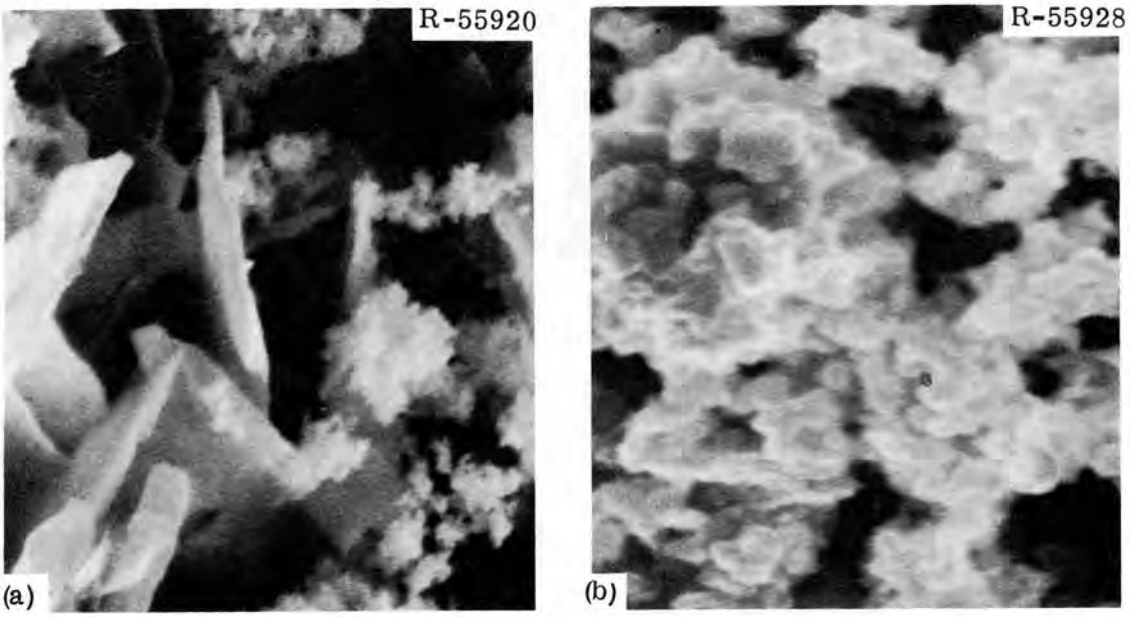


Fig. 14. A-5331-116-4 UO_2. (a) 7500×. (b) 20,000×.

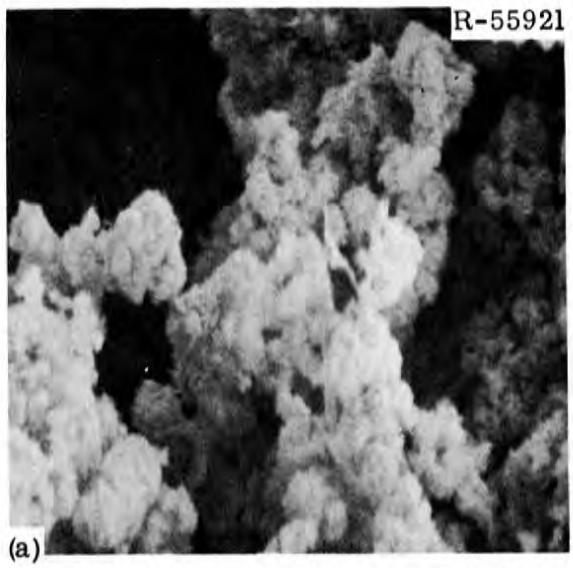
material is better revealed in (b) (20,000×), where individual particles can be seen.

A-5331-118-1 (UO_2)

Figure 15 reveals in this sample (a) a comparatively well separated material and (b) some platelet-like material.

A-5331-118-2 and A-5331-118-3

The comparatively well separated character of A-5331-118-2 is revealed in Fig. 16 (1500×). A-5331-118-3 was also well separated, although not as much as A-5331-118-2. Some of the individual particles can be seen in Fig. 17 (10,000×). The uranate precursors of these powders were particularly free flowing and easy to handle, as noted above.



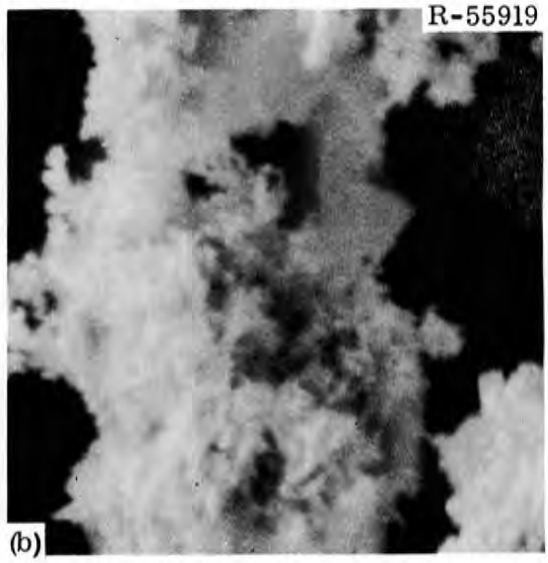


Fig. 15. A-5331-118-1 UO_2. (a) 1500×. (b) 7500×.

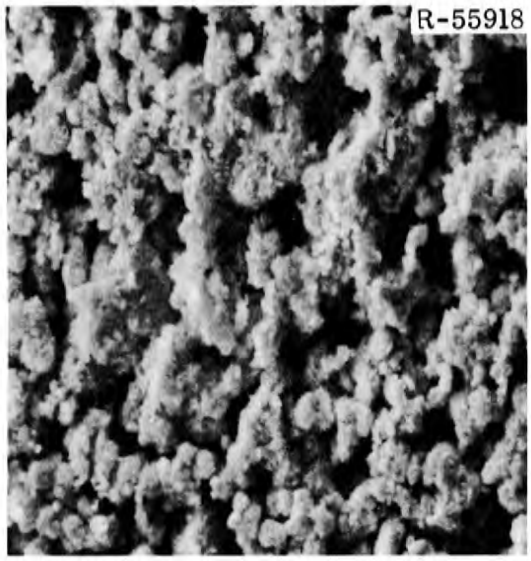


Fig. 16. A-5331-118-2 UO_2. 1500×.

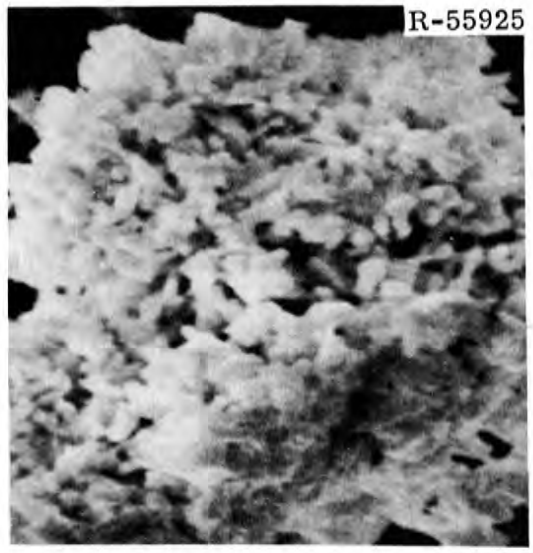


Fig. 17. A-5331-118-3 UO_2. 10,000×.

Summary of SEM Examination of Uranate and UO_2 Powders

Two morphologies of uranate powder were revealed in the single precursor that was examined. Two morphologies of UO_2 powder were also revealed, and these may be related to the precursor. However, they may well be caused by a still unexplained surface area reduction during the hydrogen treatment. The two morphologies of the UO_2 help explain the

thermal behavior on exposure to air described in the section on Stabilization of UO_2 by Control of Surface Area. Free-flowing uranate powder yielded UO_2 that appeared more dispersible than the non-free flowing; this conclusion is qualitative and needs verification. The smallest particles resolved differ from a calculated particle size by a factor of 3, even ignoring the small surface area morphologies.

EXTRAPOLATION OF INVESTIGATION TO PRODUCTION CONDITIONS

A uranium concentration of 100 g U/liter of uranyl nitrate solution has been used (about 0.42 M in U). An increase to 130 g U/liter of uranyl nitrate solution (to 0.56 M in U) would result in a decrease in surface area of the ammonium uranate, according to data by Dembinski et al.[19] The concentration effect observed, however, is considerably less than the effect of digesting during precipitation and is about the same as the effect on the uranate powder of raising the temperature of precipitation to 70°C. We found that the effect on the final UO_2 of raising the temperature from 25 to 60°C raised the surface area of the UO_2 by only 0.07 m^2/g. Thus, we conclude that raising the concentration of the U in solution will have a negligible effect.

Free acid effects were investigated; increasing the acid concentration from 0.4 to 1.4 M raised the final UO_2 surface area by 0.74 m^2/g. We conclude that lowering the acid content to 0.1 M would lower the surface area of the product UO_2.

In the experiments reported in Table 6, p. 32, samples were taken from the center of the furnace, since these represent the 600°C region, which yields the desired surface area. For production of $^{235}UO_2$ to simulate $^{233}UO_2$ production, a higher temperature was used so that the average surface area would be approximately 6 m^2/g. A furnace center temperature of 680°C was used to yield an average of 600° overall. In Table 7 the parameters discussed above are tabulated along with those of test batches of enriched material. Note that these parameters are not

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[19] W. D. Dembinski, A. Deptula, and S. Reykowski, Nukleonika 11, 567–574 (1966).

Table 7. Test of Extrapolation of Test Conditions to Production Conditions

	CS-5	CS-7	PS-1	PS-2	PS-3
Conversion Parameters					
Uranium concentration, g/liter	100	100	120	120	120
Free acid, N	0.4	0.1	0.1	0.1	0.1
Precipitation temperature, °C	45	50	30–50	30–50	30–50
Reduction temperature (center)	600	600	680	680	680
Powder Characteristics					
U total, wt %	87.1	87.3	87.5	87.89	87.96
O/U ratio	2.08	2.05	2.06	2.04	2.06
Surface area, m^2/g	8.56	7.77	5.29	3.75[a]	4.74[b]
Tap density, g/cm^3	1.65	1.58	1.88	1.97	
Moisture, wt %	0.23	0.19	0.04	0.02	0.24

[a] In PS-Lot 2 the boats were taken directly into the air without passing down the stabilizer. One end of each of two boats ignited. Since this was the high surface end, the low result here reflects this loss.

[b] One end of one boat burned, which lowers the average surface area somewhat. Most of the material was passed down the stabilizer.

directly comparable to those in Table 6. Results reported in Table 6 were taken from the center of the furnace; results reported in Table 7 are the average of blended batches.

The results in Table 7 indicate our extrapolation, discussed above, of test conditions to production conditions. Note that the surface area is particularly low on PS-2. This arises because some of the high surface fraction in the boats ignited (it was removed directly from the furnace) and was discarded. A little was also lost in PS-3. We were attempting to obtain an average surface area of 6 m^2/g. It appears that we have raised the furnace temperatures just a little too high. Otherwise, the results are all we expect and seem to verify the validity of our total analysis.

BLENDING STUDIES

Following stabilization and sieving of the $^{233}UO_2$ to be produced as well as the stand-in $^{235}UO_2$ already produced, individual batches are blended so that the entire lot will be homogeneous. To accomplish this, a V blender is used with a rotating speed of 25 ± 2 rpm.

Gray[20] has shown that for two free-flowing powders of comparable particle size and density, homogeneity is attained within 3% after 100 turns in a V blender. Further, no significant improvement is attained by further blending, even after 1000 turns.

To be sure that Gray's study applied to blending of UO_2, we investigated the efficiency of the 11-liter V blender by withdrawing samples from it after blending times of 15, 30, and 45 min. The samples were analyzed for U(VI) and surface area. The results are presented in Table 8.

[20] J. B. Gray, Chem. Engr. Progr. 53, 25J–32J (1957).

Table 8. Effect of Blending Time on UO_2 Powder Homogeneity[a]

Sample[b]	Blending Time (min)	Surface Area[c] (m^2/g)	U(VI)[d] (wt %)
B-15-1	15	5.13	4.99
B-30-1	30	5.26	5.07
B-45-1	45	5.25	5.03
B-15-2	15	5.22	5.73
B-30-2	30	5.28	5.67
B-45-2	45	5.61	5.60

[a] A 2-kg batch of $^{235}UO_2$ was blended at a speed of 25 rpm.

[b] The sample No. 1 or 2 denotes the side of the blender from which the sample was withdrawn.

[c] Surface areas were determined by the BET method.

[d] U(VI) was determined coulometrically. The first three analyses were performed on Thursday of one week; the second three analyses were performed on Tuesday of the following week.

The surface area determinations indicate no appreciable difference in the homogeneity of the material after a blending period of 15 min. This is further emphasized by the 150°C gradient within the furnace, which results in a surface area range from 9 to 2 m^2/g, depending on the location in the boat. The U(VI) determinations appear to indicate that mixing is good in each arm of the blender but not between the arms; however, the differences in the values could be attributed to the pickup of oxygen as a result of the delay in making the determinations (see footnote d, Table 8).

ACKNOWLEDGMENTS

Assistance is gratefully acknowledged from D. R. Cuneo and L. D. Hulett, who performed the scanning electron microscope examination. Timely discussions with J. R. Parrott, T. F. Scanlan, and R. Lloyd contributed materially to the progress of the project. The assistance of T. L. Douglass and D. E. Rosson during the design and installation of equipment was of material assistance.

APPENDIX

$^{233}UO_2$ Powder Process Outline

This section contains the process outline for production of $^{233}UO_2$. It was constructed as a joint effort between ORNL and BAPL personnel and was based on the conclusions drawn from this parametric study, modified by consideration of quality control and acceptable manufacturing procedures for the production line. Those persons involved in drawing up the outline were R. E. Brooksbank, Section Chief, Pilot Plant Section; T. L. Douglass, J. M. Leitnaker, W. T. McDuffee, Jr., J. R. Parrott, Assistant Section Chief, Pilot Plant Section; and J. W. Snider (all of ORNL); and T. F. Scanlan and R. Lloyd of BAPL.

1. SCOPE

1.1 This document establishes the processing procedure and parameters for conversion of purified uranyl nitrate to uranium dioxide powder. The UO_2 powder produced shall meet all of the agreed specification.

2. MATERIALS

2.1 Purified uranyl nitrate.

2.2 Anhydrous NH_3 (gas): 99.98% NH_3 minimum, Grade A.

2.3 H_2: 99.5% H_2 minimum.

2.4 Ar: 99.995% Ar minimum.

2.5 All water used in the conversion process shall be deionized or distilled and shall have a minimum specific resistance of 3.5×10^5 ohms.

2.6 All other materials which come in contact with the uranium during processing shall not degrade the UO_2 powder produced to such an extent that the powder fails to meet the requirements of specifications.

3. FACILITIES AND EQUIPMENT

3.1 Facilities housing the conversion equipment shall be initially free and maintained free of chemical and particulate contaminants (particularly uranium isotopic contaminants) which may degrade the UO_2 powder being produced. Specifically, no material other

3.1 (continued)

than purified ^{233}uranium compounds, meeting isotopic and purity requirements, shall be processed within the facilities during the execution of the ^{233}U conversion program.

3.2 All equipment used in the conversion process shall be initially free and maintained free of chemical and particulate contaminants (particularly uranium isotopic contaminants) which may degrade the UO_2 powder being produced. Specifically, the equipment shall not be used to process any material other than purified ^{233}U compounds which meet the isotopic and purity requirements during the execution of the ^{233}U conversion program.

3.3 All control measuring and monitoring devices shall comply with agreed calibration system requirements.

3.4 All in-process analytical procedures shall be submitted to and approved by the purchaser prior to production use.

4. PROCESS

4.01 Each powder production batch shall be uniquely identified so that its history may be traced from any operation in the conversion process.

4.02 The conversion process and process parameters shall not be changed or modified, in whole or in part, without prior formal consent of the purchaser.

4.03 Process control shall be verified by determining the U^T, U^{+6}, and surface area of a sample of the first batch of each 5 batch increment. Results of the analyses shall confirm that the powder tested meets the specification requirements for these attributes before each 5 batch increment is charged to the blender.

4.1 Precipitation Preparation

Manufacturer analyses shall confirm that the purified uranyl nitrate solution in the purification product holding tank has the following properties.

*4.1.1 Impurity and U isotopic concentrations consistent with the requirements specified.

*4.1.2 A uranium concentration of 120 ± 10 grams/liter of solution.

*4.1.3 A HNO_3 free acid concentration of $0.3^{+0.1}_{-0.2}$ N.

4.1.4 A solution temperature of 30 ± 15°C.

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*Critical parameter.

4.2 Precipitation of Ammonium Uranate

4.2.1 Ammonium uranate shall be batch precipitated by bubbling NH_3 (gas) into recirculating uranyl nitrate solution (from Section 4.1, above).

4.2.1.1 The batch size shall be 1000 ± 200 g of uranium.

*4.2.1.2 The NH_3 flow rate shall be 0.5 ± 0.1 moles/min.

*4.2.1.3 The precipitation is finished when a pH of 8.25 ± .25 reached.

*4.2.1.4 The solution temperature during precipitation shall be $50\ ^{+10}_{-20}$°C

*4.2.1.5 The recirculation rate of the solution during precipitation shall be 4.5 ± 1.5 system vols/min.

4.3 Recovery of Ammonium Uranate

4.3.1 Ammonium uranate precipitate shall be recovered from the slurry (Section 4.2, above) by centrifugation.

4.3.1.1 The centrifuge batch size shall be 1000 ± 200 g U (in slurry)

4.3.1.2 The centrifuging force shall be 1800 ± 600 × g.

4.3.1.3 The centrifuging time shall be a minimum of 5 minutes after all material is added to the centrifuge, but not longer than 1 hour.

4.4 Drying Ammonium Uranate

4.4.1 The ammonium uranate (from Section 4.3, above) shall be batch dried using a microwave oven.

4.4.1.1 The batch size shall be 1000 ± 200 g of uranium (as uranate).

4.4.1.2 The drying temperature shall be $100\ ^{+15}_{22}$°C.

4.4.1.3 The drying time shall be determined by reflected power, which will be such that a moisture content of 6 ± 4 wt % H_2O remains in the uranate cake.

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*Critical parameter.

4.5 Sieving Ammonium Uranate

4.5.1 The dried ammonium uranate (from Section 4.4, above) shall be passed through a 35 mesh sieve.

4.6 Reduction of Ammonium Uranate to Uranium Dioxide

4.6.1 The sieved ammonium uranate (from Section 4.5, above) shall be reduced to uranium dioxide by calcining in hydrogen.

4.6.1.1 Calcining shall be performed in a continuous multi-zoned furnace with an Inconel muffle using Inconel furnace hardware.

*4.6.1.2 The depth of ammonium uranate loaded into each furnace boat shall not exceed 1/2 in. evenly spread across the bottom.

*4.6.1.3 Each boat of ammonium uranate shall be subjected to the following reduction cycle:

a. Heated from ambient to 575 ± 25°C at 200 ± 25°C/hr in Ar.

b. Moved across a gas barrier into H_2 at 625 ± 25°C.

c. Held at 625 ± 25°C for 6 ± 0.5 hr in H_2.

d. Furnace cooled in H_2 to 50 ± 25°C.

e. Cooled in Ar in water-cooled furnace region to ambient temperature.

*4.6.1.4 The hydrogen flow rate shall be a minimum of 0.035 system volumes/min.

4.7 Stabilization of Uranium Dioxide Powder

4.7.1 The uranium dioxide powder (from Section 4.6, above) shall be stabilized by controlled exposure to air.

4.7.1.1 The stabilizing equipment shall produce a moving bed of powder blanketed by a concurrent flow of humidified argon meeting a counter current flow of humidified air.

4.7.1.2 Stabilization shall be performed at ambient temperature.

*Critical parameter.

4.7.1.3 Powder bed depth shall not exceed 1/4 in.

4.7.1.4 Powder flow rate shall not exceed 25 g/min.

4.7.1.5 Argon velocity shall be 2 ± 1 cm/sec.

4.7.1.6 Air velocity shall be 2 ± 1 cm/sec.

4.7.1.7 The relative humidity of both the argon and air shall be saturated at ambient temperature.

4.8 Sieving and Sampling Uranium Dioxide

*4.8.1 Stabilized uranium dioxide powder (from Section 4.7, above) shall be passed through a 100 mesh sieve to break up powder agglomerates.

4.8.2 A representative 5 gm sample of sieved UO_2 powder of the first of each five batches shall be withdrawn for process control verification at this point (ref. 4.03). Each 5 consecutively produced batches of powder shall be held at this operation until process control is verified.

4.9 Powder Blending

4.9.1 All stabilized, sieved powder shall be blended in a "V" blender to produce a homogeneous powder lot.

4.9.1.1 The powder lot size shall be set by the purchaser (not to exceed 20 kg U).

4.9.1.2 The blending time shall be 1 ± 0.5 hr.

4.9.1.3 The "V" blender speed shall be 25 ± 2 rpm.

4.9.1.4 The powder batches comprising each blender powder lot shall be permanently recorded.

4.9.1.5 Samples shall be drawn from each blended powder lot for analysis and certification to the agreed specifications.

5. EXCEPTIONAL MATERIAL

5.1 Repair of Material

Material not converted to UO_2 according to this process outline shall be returned to the purification system for dissolution. This statement is intended to specifically forbid any repair of off-spec material.

*Critical parameter.

5.2 Unusual or Unexpected Results

An unusual or unexpected results shall be reported to purchaser. The purchaser's concurrence shall be obtained prior to further processing of the affected material.

6. PACKAGING AND SHIPPING

6.1 Packaging

6.1.1 Each powder lot shall be packaged (primary container) in stainless steel screw-top cans supplied by the purchaser.

6.1.1.1 Each primary container shall contain not more than 500 g of ^{233}U.

6.1.1.2 Each primary container shall exhibit the powder lot identity, can number of that lot, tare weight, gross weight, net powder weight, and purification date.

6.1.1.3 No more than two primary containers shall be sealed in each isotope can.

6.1.1.4 No more than two isotope cans shall be placed in each approved shipping container.

6.1.1.5 Each shipping container shall exhibit the purification date of the container material.

6.2 Shipping

6.2.1 All shipping containers shall be transported in accordance with applicable DOT regulations.

7. PROCESS AND EQUIPMENT LIMITS

7.1 Production equipment shall have the capacity to produce the following process parameter ranges:

Parameter	Range
U concentration (g/l)	90–130
Free acid (N)	0.1–0.5
Precipitation temperature (°C)	Ambient–65
NH_3 gas flow rate (mole/min)	0–1
Precipitation recirculation rate (sys vol/min)	0–6
Centrifuge force (nominally 1800g)	None

Parameter	Range
Centrifuge time (min)	> 5
Drying temperature (°C)	25–120
Drying time (min)	0–120
Ammonium uranate powder size (mesh)	Minus 35
Ammonium uranate preheat temperature in Ar (°C)	Ambient–600
Ammonium uranate reduction temperature in H_2 (°C)	500–900
Heat-up rates (both furnace zones) (°C/hr)	50–250
H_2 flow rate (sys vol/min)	0.02–0.4
Stabilization temperature (°C) (nominally ambient)	None specified
Stabilization powder flow rate (g/min)	0–30
Stabilization Ar velocity (cm/sec)	0–3
Stabilization air velocity (cm/sec)	0–3
Stabilization Ar and air relative humidity (%)	0 or saturated at ambient temperature
Uranium dioxide powder size (mesh)	Minus 100
Blend lot size (kg)	0–20
Blending time (hr)	0–8

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