SOME PREPARATION METHODS AND PHYSICAL CHARACTERISTICS OF UO_2 POWDERS

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Methods of preparation of uranium dioxide powders having a wide range of physical properties are discussed. The effects of chemical and mechanical processes, temperature of preparation and O/U ratio on the density, surface area, porosity, crystallite size, and particle size distribution of the UO_2 are determined. The results of a microscopic study reveal that the shape and structure of the UO_2 particles depend upon their method of preparation.

SOME PREPARATION METHODS AND PHYSICAL CHARACTERISTICS OF UO_2 POWDERS

J. C. Clayton and S. Aronson

The oxide UO_2 has become of considerable importance as a nuclear fuel in the field of atomic power. Published data on the surface area, density, porosity, crystallite size, microstructure, and sinterability of this compound show wide variations (Refs 1-5). Considerable evidence shows that the characteristics of powders, such as the uranium oxides, are determined largely by their preparative history. For example, it was ascertained that the density and surface area of a UO_2 preparation depend upon the density and surface area of the substance from which the UO_2 was prepared (Ref 1). Therefore, a study was undertaken to find the relationships between the method of preparation of UO_2 and its physical properties. Information was sought regarding the effects of chemical and mechanical processes on microstructure, density, surface area, porosity, crystallite size, and particle size distribution.

EXPERIMENTAL METHODS

Preparation of UO_2 Powders

UO_2 was made by several oxidation and reduction methods, including hydrogen reduction of the higher uranium oxides (UO_3 , $UO_3 \cdot 2H_2O$, $UO_3 \cdot H_2O$, and U_3O_8) at temperatures ranging from 500-1700°C as well as steam and air oxidation of uranium hydride and uranium metal. (The methods have been summarized in Table I.) These UO_2 powders were non-pyrophoric in all cases. UO_2 was also prepared from precipitated U(VI) salts. The precipitation of ammonium diuranate by gaseous ammonia, ammonium hydroxide, urea, and ammonium carbonate was studied in detail. The formation of uranyl oxalate and uranium peroxide was also investigated. A series of these precipitated powders were converted into UO_2 either directly by heating in hydrogen or by first pyrolyzing the powders in air to form U_3O_8 and then reducing with hydrogen. In most cases the products were pyrophoric, oxidizing to a black material with O/U ratios ranging from 2.22 to 2.34. More stringent reduction conditions, however, gave stable brown powders. The preparation procedures are described in detail in Appendix I.

TABLE I
UO₂ PREPARATION METHODS

Method of Preparation	Reaction Conditions		O/U Ratio	Color
	Temperature (°C)	Time (hr)		
High pressure (2200 psig) steam oxidation of uranium	343	6-72	1.85-1.99	black
Controlled low pressure (3.5-7.5 psig) steam oxidation of uranium	150-250	8-16	2.01-2.05	black
Uncontrolled low pressure (3.5-7.5 psig) steam oxidation of uranium	250-450	2-8	2.05-2.20	black
Air pyrolysis of UO ₂ (NO ₃)·6H ₂ O to UO ₃ ; hydrogen reduction of UO ₂	480-1650	2-50	2.01-2.03	brown
Fluidized bed denitration and UO ₃ reduction	700	6	2.07	black
Hydrogen reduction of UO ₃ ·2 H ₂ O	850	6	2.01	brown
Hydrogen reduction of UO ₃ ·H ₂ O	1700	2	2.01	grey-black
Air pyrolysis of uranium, UO ₃ and UO ₂ to U ₃ O ₈ ; hydrogen reduction to UO ₂	800	16	2.01-2.02	brown
Hydrided-steam oxidation of uranium	150-400	12-16	2.03-2.05	red-brown
Hydrided-air oxidized uranium; hydrogen reduction of U ₃ O ₈ to UO ₂	150-800	16	2.02	red-brown
Direct hydrogen reduction of uranium peroxide	900	4-56	2.02-2.08	brown
Air ignition of uranium peroxide to U ₃ O ₈ ; hydrogen reduction to UO ₂	900	56	2.02	cocoa-brown
Direct hydrogen reduction of uranyl oxalate	900	64	2.01	red-brown
Air ignition of uranyl oxalate to U ₃ O ₈ ; hydrogen reduction to UO ₂	900	62	2.03	dark brown
Direct hydrogen reduction of ammonia-precipitated diuranate	900	56	2.05	light brown
Air ignition of ammonia precipitated diuranate to U ₃ O ₈ ; hydrogen reduction to UO ₂	900	80	2.13	green-brown
Direct hydrogen reduction of ammonium hydroxide precipitated diuranate	850-950	4-32	2.07	brown
Air ignition of ammonium hydroxide precipitated diuranate to U ₃ O ₈ ; hydrogen reduction to UO ₂	800	34	2.14	light brown
Direct hydrogen reduction of urea precipitated diuranate	775-800	16	2.08	grey-brown
Air ignition of urea precipitated diuranate to U ₃ O ₈ ; hydrogen reduction to UO ₂	900-1050	32	2.11	grey-brown
Direct hydrogen reduction of ammonium carbonate precipitated diuranate	900-1000	56-64	2.05-2.06	dark brown
Air ignition of ammonium carbonate precipitated diuranate to U ₃ O ₈ ; hydrogen reduction to UO ₂	900-1000	110-150	2.04-2.05	brown

Chemical Analyses

The UO_2 powders were analyzed for total uranium, U(IV), U(VI), and water content. The quantity of U(VI) was determined by a modification of a polarographic method of Tishkoff (Ref 6) which is described in Appendix II. Total uranium and U(IV) were determined volumetrically by titration with standard potassium dichromate. The moisture content was obtained by direct absorption in magnesium perchlorate. The analytical methods are described in detail in Refs 7 and 8. With these procedures, the O/U ratios of the powders were determined with an accuracy of ± 0.01 or better. Spectroscopic analyses indicated that metallic impurities were less than 0.1%.

X-Ray Analyses

X-ray patterns were made on film using a 114.6 mm powder camera and copper K_α radiation. The samples were extruded through a 20-mil tube after dilution with starch and the addition of a collodion binder.

Microstructure Study

The uranium precipitates were dispersed in ethylene glycol and examined microscopically with transmitted light. The uranium oxide powders were mounted in a plastic medium and polished with abrasives for cross section examination. Viewing was accomplished with reflected light. The techniques are fully described in Appendix III.

Density Measurements

Bulk densities were measured according to a specified method of loading a designated container. A tared brass container of known volume (4.84 cc) was filled with UO_2 to overflowing and weighed after leveling off the powder. The powder was added through a modified Hall flowmeter with a 0.281-in. diam orifice. The reproducibility of this procedure was within $\pm 1\%$.

"Real" and "liquid" densities were measured by helium and CCl_4 displacement. The general techniques of density measurement are well known (Refs 9 and 10). However, the apparatus used for the displacement measurements differs from others used previously and is described in detail in Appendix IV. The precision of the density values obtained by helium displacement for UO_2 powders having volumes of 2 cc was within $\pm 0.5\%$. The precision increased with increasing sample size. The UO_2 powders were degassed at a maximum pressure of 10^{-5} mm Hg for 1 hr at 400°C . The precision of the density measurements obtained by liquid displacement was within $\pm 0.2\%$. Samples were dried in vacuo (100 microns) for 15 hr at 70 - 100°C and degassed at room temperature. Density values obtained using carbon tetrachloride, benzene, ether, and water were approximately the same. Carbon tetrachloride was chosen as the standard displacing liquid.

Surface Area Measurements

Total surfaces were determined by volumetrically measuring the adsorption of nitrogen on UO_2 at liquid nitrogen temperature. Both the conventional BET (Brunauer, Emmett, and Teller) method and the Innes method were used. In the BET procedure, adsorption measurements were carried out by adding gas in increments and allowing it to equilibrate with the adsorbent after each addition (Refs 11 and 12). Ten minutes were allowed for pressure equilibration before readings were taken. Four experimental points at relative pressures between 0.05-0.3 were obtained for the BET plot. The Innes surface area method, which is essentially a rapid one-point BET method, involves the use of a constant, very small flowrate of gas into the adsorbent section. Equilibrium pressure is approximated and the amount of gas adsorbed is proportional to time elapsed (Ref 13). The apparatus used differed slightly from that of Innes and is described in Appendix V. Sample weights of UO_2 were 10-30 g. Standard techniques of degassing in vacuo the UO_2 samples at 400°C for 1-4 hr and U_3O_8 samples at 200°C for 1 hr were adopted. Chemical analyses showed that no oxidation occurred on degassing. The uranium precipitates and UO_3 were degassed in vacuo at 80 - 100°C for 2 hr. Values

obtained on UO_2 samples treated in a similar manner agreed within $\pm 5\%$. Krypton and nitrogen adsorption measurements gave comparable results on UO_2 powders in the region of $1 \text{ m}^2/\text{g}$ where both techniques were applicable (Ref 14).

Air permeability methods were used to give an estimate of the areas of the external surfaces of the uranium oxides. An apparatus based on the method of Gooden and Smith (Ref 15) was used for the coarser powders with external surface areas of less than $6 \text{ m}^2/\text{cc}$. In this instrument, air is forced by a pump through the packed sample at constant flow, and the recorded pressure drop along the sample is a measure of the permeability and, thus, of the external surface. For the finer oxide powders, the method of Carman and Malherbe (Ref 16) was used. In this technique, a self-supporting pellet of UO_2 is formed in an accurately machined tube with a small hand press. The volume of air flowing through the sample is directly measured with a graduated tube. This apparatus is applicable for measuring powders with external surface areas ranging from $3\text{-}60 \text{ m}^2/\text{cc}$.

Particle Size Distribution Analyses

An air sedimentation apparatus* was used to obtain particle size distributions for some of the uranium oxides. A cloud of well-dispersed powder particles is introduced at the top of a pressure-tight, 220-cm, thermally insulated, sedimentation column. The particles fall because of the action of gravity, and are collected on the pan of an automatic balance which continuously records the cumulative weight collected as a function of time. These data are converted into a particle size distribution curve plotted with a template incorporating Stoke's law. For a nonspherical particle, the size measured is the diameter of a sphere which falls at the same rate. A surface area can be calculated from the size distribution.**

Thermal Analyses

An apparatus was constructed similar to that of Mauer (Ref 17) for the simultaneous recording of weight-change and differential thermal analysis curves. Platinum-platinum, 10%-rhodium thermocouples were used in platinum sample holders. The furnace was wound with platinum wire. The heating rates were $4\text{-}6^\circ\text{C}/\text{min}$. Alumina served as the reference material.

RESULTS AND DISCUSSION

X-Ray Analyses

An investigation was made to determine whether the uranium oxides and their parent compounds could be characterized as to method of preparation by their X-ray diffraction patterns. Samples of ammonium diuranate, UO_3 , U_3O_8 , and UO_2 prepared by various methods were examined.

The crystallite size of UO_2 prepared by hydrogen reduction of UO_3 and U_3O_8 varied with the temperature of reduction. UO_2 prepared at 500°C had broader powder lines than the material made at higher temperatures, indicating a smaller crystallite size. At higher reduction temperatures, the powder patterns became sharper which suggested crystallite growth. Broad powder lines were also observed for UO_2 which had been prepared by the steam oxidation of uranium. This is consistent since the steam oxidation temperatures were below 450°C . In addition U_3O_8 , which was made by ignition in air at 800°C of the UO_2 prepared by high pressure steam oxidation, yielded the sharpest U_3O_8 X-ray pattern, showing that some crystallite growth occurred during oxidation. The crystallite sizes of uranium oxide powders, thus, depend more on the temperature of preparation than on the method of preparation. This conclusion is in agreement with the work of Anderson, et al. (Ref 1).

* Sharples Micromerograph, Sharples Corporation Research Laboratories, Bridgeport, Pa.

** Operation Manual for the Sharples Micromerograph (1957)

The crystallite sizes of two representative UO_2 samples were accurately measured. The X-ray patterns for these samples were obtained on a double crystal spectrometer, and Fourier analysis of the 531 peaks was used to determine the average crystallite size. UO_2 prepared by high pressure steam oxidation of uranium at 343°C had a crystallite size of $180 \pm 20 \text{ \AA}$. Mallinckrodt PWR Core I UO_2 , made by hydrogen reduction of UO_3 at 800°C , had a crystallite size of $900 \pm 115 \text{ \AA}$.

It had been reported that U_3O_8 was the chief product in the steam oxidation of uranium above 300°C and also that U_3O_8 was not found even at 1000°C (Ref 4). To clarify this apparent discrepancy, mechanical mixtures of UO_2 and U_3O_8 were prepared and analyzed by the X-ray method. It was found that at least 10% U_3O_8 must be present in the UO_2 to be detected. Since U_3O_8 could not be detected in those samples prepared by steam oxidation with O/U ratios as high as 2.2 (corresponding to 30% U_3O_8), it was inferred that at least a large part of the excess oxygen is homogeneously dissolved in the UO_2 lattice and is not present as U_3O_8 .

Microstructure

Microscopic examination of the UO_2 powders indicated that their particle size, shape, and microstructure depend on their method of preparation. These diverse characteristics are illustrated in Figs. 1-13. The particle sizes ranged from tenths of microns up to several millimeters. The shapes included spheres, needles, plates, and irregularly curved and angular particles. The internal particle structures varied from nearly solid chunks to very loose spongy masses and included cluster-like and cored structures.

As shown in Figs. 1 and 2, steam oxidation of uranium metal foil produced powders which were, in general, less porous in appearance than oxide prepared by the reduction methods (Figs. 3-12). In particular, the coarse dense particles shown in Figs. 1A and 2A illustrate the conclusions made from high density and low surface area measurements. (Refer to the later paragraphs of this article on density and surface area measurements.) The form of the uranium metal also has an effect on the particle structure. Steam oxidation of finely divided uranium powder resulted in a finer particle structure (Fig. 2C) than was produced from uranium foil (Fig. 2A). The same effect was also found for UO_2 powders obtained by hydrogen reduction of U_3O_8 prepared from uranium powder and foil (Fig. 3).

The UO_2 powders prepared by the high pressure steam oxidation method were of two types—one contained thin, sheet-like particles (Fig. 1B), the other was composed of more massive and angular particles having numerous cracks (Fig. 1A). The cause of this difference in particle structure is not known. The low pressure steam oxidation method also resulted in two particle types. In this case, however, the difference can be attributed to the reaction conditions. The UO_2 prepared by controlled oxidation contained needles and plates having sharp edges (Fig. 2A) and its gross appearance is consistent with its very low surface area. The oxide powder made by uncontrolled oxidation was spongy in appearance (Fig. 2B) and had a higher surface area.

Mallinckrodt PWR Core I UO_2 , made by reduction of UO_3 , was composed of roughly spherical porous particles with a cluster-like structure. Figure 5A shows its general shape and porous structure. Little variation was found in general structure with sieve size (Fig. 4), which is consistent with surface area and density measurements.* The distinctly different microstructure of Mallinckrodt oxide prepared from ammonium diuranate is shown in Fig. 5B. The particles reveal a variety of irregular shapes and sizes. When Mallinckrodt PWR Core I UO_2 was ball-milled, the cluster-like structure was broken down, and the individual units were fractured to some extent (Fig. 5C). The breakup of the large agglomerates by the comminution treatment was confirmed by the gas adsorption surface area measurements

* Refer to the later section of this report titled Surface Area Measurements.

UO₂ prepared by hydrogen reduction of ball-milled UO₃ was similar in structure to the Mallinckrodt PWR Core I powder but its particle size was somewhat finer, which is in agreement with its higher surface area (Fig. 6B). The particle size showed a marked dependence on the temperature of reduction. Surface area and density measurement* as well as the microstructure (Fig. 6) indicate a considerable increase in particle size and a coalescence of pores with increase in reduction temperature. A similar effect was observed for UO₂ preparations made by reduction of both UO₃ and U₃O₈ (Ref 1). The higher the reduction temperature, the coarser the particle structure.

UO₂ particles prepared by the spray denitration technique were rounded and had a cored particle structure (Fig. 7A). Their microstructure shows some indication of accessible internal porosity which would explain their relatively high density and surface area. UO₂ particles obtained by reduction of the hydrothermally grown UO₃·H₂O crystals were large-grained rhombahedra (Fig. 7B), which showed a considerable amount of closed porosity consistent with their low density and surface area. The parent UO₃ particle shape was essentially retained in both of these processes.

When UO₂ powders were air oxidized to U₃O₈ and subsequently reconverted to UO₂ by hydrogen reduction, some of the original microstructure was preserved (Fig. 8). However, the major effect was the breakup of the larger agglomerates to produce a superficially finer powder. The small change in specific surface area that occurred indicates that the oxidation process did not fracture the more fundamental particle units composing the agglomerate.

Microscopic examination of ammonium diuranate crystals produced by addition of ammonium hydroxide to uranyl nitrate solution, showed a wide range of irregular shapes and sizes (1-600 microns). Ammonium diuranate crystals obtained from the urea reaction varied in size but were more uniform (roughly spherical) in shape. Precipitation from ammonium carbonate medium yielded uniform spherical particles. Very fine minute diuranate particles were obtained with gaseous ammonia. These differences in crystal appearance may be attributed to the mechanism of precipitation. Ammonium hydroxide gives an immediate precipitate even when added dropwise, whereas the slow decomposition of urea results in the slow homogeneous generation of ammonium hydroxide from within the solution. Ammonium carbonate first causes the precipitation of ammonium uranyl carbonate which is then decomposed by boiling to form ammonium diuranate.

A comparison of photomicrographs of the uranium oxides obtained from these diuranate powders shows similar differences in crystal appearance. UO₂ prepared from ammonium-hydroxide-precipitated diuranate varied in size and shape (Fig. 9). Urea-precipitated diuranate yielded oxide with somewhat less particle structure variation (Fig. 10). However U₃O₈ and UO₂ made from ammonium diuranate precipitated with ammonium carbonate were composed of fairly uniform spheres (Fig. 11). In these preparations, the microstructure of the original ammonium diuranate is retained on conversion to U₃O₈ and UO₂. However, the microstructure of the uranium oxide powders prepared from ammonia-precipitated diuranate, uranyl oxalate, and uranium peroxide was distinctly different from that of the starting uranium precipitates. The U₃O₈ and UO₂ obtained from diuranate precipitated with gaseous ammonia were massive and angular in appearance (Fig. 12) while the oxides made from uranyl oxalate were acicular (Fig. 13). The fact that the U₃O₈, the U₃O₈-reduced UO₂, and the precipitate-reduced UO₂ have almost identical microstructures can be used as evidence of a reduction mechanism for the uranium precipitates, in which they are first converted into U₃O₈ which is subsequently reduced to UO₂.

Density Measurements

The theoretical densities of UO₂, U₃O₈, and UO₃ are 10.97, 8.39, and 8.34 g/cc (Ref 4). This "ideal," crystallite, or X-ray density is calculated from the size of the unit cell and the atomic

Refer to the later sections of this report titled Density Measurements, Surface Area Measurements.

weights of the constituents, assuming that all lattice points are occupied. However, experimental density values for the uranium oxides vary over a wide range, depending on the experimental technique and the method of preparation (Ref 4). Density data, obtained from the displacement of a fluid that can penetrate all pores and capillaries of a solid down to molecular dimensions, are termed "real" densities. Closed pores, which are voids completely surrounded by the solid, are arbitrarily considered as part of the "real volume" of the material. The helium atom has a small molecular diameter which enables it to penetrate into very fine pores. In addition, there is negligible adsorption of helium on solids at room temperature (Ref 18). Therefore, densities obtained by helium displacement most closely conform to the definition of "real" densities. Measurements obtained by liquid displacement are usually lower because the liquid does not completely penetrate the pores of the solid (Ref 18).

The bulk density of a powder is defined as the ratio of mass-to-volume measured according to a standard method of filling a container of specified dimensions. The bulk density is of particular importance in powder metallurgy since in most pressing operations the dies are filled by volume. In addition, the length of the compression stroke and, thus, the depth of the dies, depends on the bulkiness of the powder (Ref 19).

The measured densities of UO_2 powders, prepared by steam oxidation procedures, approach the theoretical value, 10.97 g/cc (see Table II). The densities obtained by liquid displacement are

TABLE II
PROPERTIES OF UO_2 PREPARED BY STEAM OXIDATION METHODS

Method of Preparation	Reaction Conditions	O/U	Density (g/cc)			Surface Area (m^2/cc)			Roughness Factor (Sg/Sp)
			He	CCl_4	Bulk	BET (Sg)	Permeability Porosity (Sp)		
High pressure steam oxidation of uranium	72-hr oxidation at 343°C and 2200 psig	1.97	10.92±0.1	10.75	2.76	12.9	0.645	3.1	4.2
Controlled low pressure steam oxidation of uranium	24-hr oxidation at 150°C and 5 psig; dried 8 hr in vacuo at 700°C	2.02	10.85±0.1	10.91	1.75	2.4	0.645	3.2	0.8
Uncontrolled low pressure steam oxidation of uranium	5-hr oxidation at 350°C and 5 psig; heated in hydrogen 5 hr at 900°C	2.03	10.92±0.05	10.85	2.47	9.0	0.645	2.7	3.3
Steam oxidation of uranium from uranium hydride	4-hr oxidation at 400°C and 5 psig; heated in hydrogen 15 hr at 700°C	2.03	10.98±0.1	10.67	1.75	22.6	0.686	5.6	4.0

slightly lower than the helium values. Thus, it is likely that these powders consist of dense granules (no closed porosity) with varying amounts (up to 3% of total volume) consisting of small open pores. This is confirmed by the microscopic studies mentioned in the previous paragraph of this report entitled Microstructure.

Density values for the UO_2 powders prepared by reduction of the higher uranium oxides are given in Table III. For the most part, the helium and liquid displacement densities are considerably below theoretical and in close agreement, indicating that these oxides contain little open porosity but an appreciable amount of closed porosity. Only in the case of powders prepared by the fluidized processes are the liquid values lower, suggesting the presence of some small open pores. When high density UO_2 prepared by the high pressure steam oxidation method was ignited to U_3O_8 and converted back to UO_2 by reduction, the real density (10.69 g/cc) of the product was still higher than the densities (10.02-10.35 g/cc) of the other U_3O_8 -reduced UO_2 powders.

In addition, as shown in Table IV, the lower the density of a UO_3 preparation, the lower the density of the resulting UO_2 . The persistence of the low density during the oxidation and reduction of MCW PWR Core I UO_2 emphasizes this point. The dependence of the density of a UO_2 preparation upon the density of the substance from which it has been made by reduction is in agreement with the work of Anderson, et al.

The relatively high real density (10.54 g/cc) of a UO_3 -reduced powder obtained from the UO_2 prepared by the fluidized bed denitration and reduction method may be caused in part by its high O/U ratio (2.07) (see Table III). In addition, the fluidization reduction process itself may have decreased the amount of closed porosity by preventing the particles from remaining in intimate contact with each other. When UO_3 made by denitration in a fluidized bed was placed in platinum boats and reduced with hydrogen, using standard techniques, the real density of the resulting UO_2 was much lower (10.13 g/cc) and the spherical shape of the particles was not retained.

The density measurements for UO_2 powders prepared by direct reduction of the uranium precipitates are listed in Table V. In general, the helium displacement density values of the UO_2 powders prepared from ammonium diuranate and uranium peroxide were close to the theoretical value, 10.97 g/cc. The liquid displacement densities were below the helium values, suggesting that these powders have varying amounts of small open pores. Densities obtained by both helium and liquid displacement for the UO_2 preparation made from uranyl oxalate were below theoretical and identical, indicating that this oxide contains no open porosity but a measurable amount of closed porosity.

As seen in Table IV, there seems to be no apparent relationship between the densities of the uranium precipitates and the densities of the resulting UO_2 powders. Thus, ammonium diuranate powders with densities of 4.82 and 5.75 g/cc yielded $\text{UO}_{2.05}$ with densities of 10.85 and 10.30 g/cc, respectively.

Densities for the UO_2 powders prepared by reduction of U_3O_8 obtained from the uranium precipitates (given in Table VI) vary over a wide range. For Mallinckrodt oxide, the helium and CCl_4 densities are high and in close agreement, indicating little porosity. Powders for which the helium and liquid displacement density values are below theoretical and in close agreement, contain little open porosity but some closed porosity. For several of the UO_2 powders, the liquid displacement densities were less than the helium values, indicating the presence of open porosity.

The data of Table IV, which indicate that the density of these UO_2 powders depends upon the density of the U_3O_8 from which they have been prepared by reduction, are consistent with the results of Anderson, et al. Two apparent exceptions, where low density U_3O_8 (7.50 and 7.53 g/cc) yielded very high density UO_2 (11.09 and 11.34 g/cc, respectively), can be partially explained as caused by the high O/U ratios (2.14 and 2.11, respectively) of these UO_2 powders. Using kerosene as a displacing liquid, Gronvold (Ref 20) found that the density of his UO_2 preparations increased from

TABLE III
PROPERTIES OF UO_2 PREPARED BY REDUCTION OF THE HIGHER URANIUM OXIDES

Method of Preparation	Reaction Conditions	O/U	Density (g/cc)			Surface Area (m^2/cc)			Roughness Factor (Sg/Sp)
			He	CCl_4	Bulk	BET (Sg)	Permeability Porosity	(Sp)	
Hydrogen reduction of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$	6 hr at 850°C	2.01	10.25±0.05	10.25	2.12	8.8	0.645	4.1	2.2
Hydrogen reduction of $\text{UO}_3 \cdot \text{H}_2\text{O}$ crystals grown hydrothermally in an autoclave	2 hr at 1700°C	2.01	10.34±0.05	10.37	4.63	0.5	0.455	0.6	0.8
Hydrogen reduction of UO_3 made by denitration in a fluidized bed	16 hr at 800°C	2.02	10.13±0.10	9.94	3.85	9.5	0.645	2.8	3.4
Fluidized bed denitration and UO_3 reduction	6 hr at 700°C	2.07	10.54±0.05	10.28	4.19	30.6	0.645	2.3	13.3
MCW PWR Core I UO_2 ; cracked ammonia reduction of UO_3	4 hr at 815°C	2.02	10.16±0.05	10.13	2.77	6.4	0.645	3.1	2.1
Air ignition of MCW UO_2 to U_3O_8 ; hydrogen reduction to UO_2	24-hr oxidation at 800°C ; 15-hr reduction at 780°C	2.01	10.35±0.10	10.32	2.21	5.4	0.645	3.3	1.6
Air ignition of high pressure steam oxidized UO_2 to U_3O_8 ; hydrogen reduction to UO_2	24-hr oxidation at 800°C ; 15-hr reduction at 780°C	2.01	10.69±0.10	10.67	1.82	4.3	0.645	3.2	1.3
Air pyrolysis of $\text{UO}_2(\text{NO}_3) \cdot 6\text{H}_2\text{O}$ to U_3O_8 ; hydrogen reduction to UO_2	48-hr oxidation at 740°C ; 16-hr reduction at 800°C	2.02	10.03±0.05	9.96	1.98	5.7	0.645	3.3	1.7
Air pyrolysis of $\text{UO}_2(\text{NO}_3) \cdot 6\text{H}_2\text{O}$ to U_3O_8 ; hydrogen reduction to UO_2	15-hr oxidation at 800°C ; 16-hr reduction at 800°C	2.01	10.02±0.10	10.07	1.93	5.8	0.645	3.0	1.9
Hydrided-air oxidized uranium; hydrogen reduction of U_3O_8 to UO_2	24-hr oxidation at 740°C ; 16-hr reduction at 800°C	2.02	10.32±0.15	10.46	1.10	9.4	0.739	5.4	1.7

TABLE IV
COMPARISON BETWEEN SURFACE AREA AND DENSITY OF UO_2 POWDERS
AND THEIR PARENT COMPOUNDS

Compound	Method of Preparation	Helium or Liquid Fluid Density (g/cc)		Total Surface Area (m^2/cc)	
		Compound	UO_2	Compound	UO_2
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Evaporation of uranyl nitrate solution	2.75	--	2.4	--
UO_3	Pyrolysis of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	7.32	10.16	9.1	6.4
UO_3	Pyrolysis of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; milled	7.66	10.36	21.2	13.8
$\text{UO}_3 \cdot \text{H}_2\text{O}$	Grown hydrothermally in an autoclave	5.84	10.34	1.1	0.5
$(\text{NH}_4)_2\text{U}_2\text{O}_7$	NH_4OH precipitation from uranyl nitrate solution	4.96	11.11	72.4	37.4
U_3O_8	Air ignition of NH_4OH precipitated diuranate at 500°C	7.50	11.09	73.2	59.9
U_3O_8	Air ignition of NH_4OH precipitated diuranate at 800°C	8.10	10.61	8.8	9.7
$(\text{NH}_4)_2\text{U}_2\text{O}_7$	Urea precipitation from uranyl nitrate solution	5.62	10.74	31.3	42.1
U_3O_8	Air ignition of urea precipitated diuranate at 500°C	7.53	11.34	74.3	60.4
U_3O_8	Air ignition of urea precipitated diuranate at 800°C	8.15	10.55	5.1	6.0
$(\text{NH}_4)_2\text{U}_2\text{O}_7$	$(\text{NH}_4)_2\text{CO}_3$ precipitation from uranyl nitrate solution	5.75	10.30	31.0	40.7
U_3O_8	Air ignition of $(\text{NH}_4)_2\text{CO}_3$ precipitated diuranate at 500°C	7.32	10.30	41.0	36.2
U_3O_8	Air ignition of $(\text{NH}_4)_2\text{CO}_3$ precipitated diuranate at 1000°C	7.94	10.46	8.6	14.1
$(\text{NH}_4)_2\text{U}_2\text{O}_7$	NH_3 precipitation from uranyl nitrate solution	4.82	10.85	93.6	40.8
U_3O_8	Air ignition of NH_3 precipitated diuranate at 500°C	8.00	10.46	102.7	58.0
$\text{UO}_4 \cdot 2\text{H}_2\text{O}$	H_2O_2 precipitation from uranyl nitrate solution	3.99	10.38	11.0	12.0
U_3O_8	Air ignition of uranium peroxide at 500°C	7.09	10.44	15.7	11.9
$\text{UO}_2(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$	Oxalic acid precipitation from uranyl nitrate solution	3.73	10.61	2.9	7.3
U_3O_8	Air ignition of uranyl oxalate at 500°C	8.22	10.68	66.0	30.4

TABLE V
PROPERTIES OF UO_2 PREPARED BY DIRECT REDUCTION OF URANIUM PRECIPITATES

Source	Reduction Conditions	O/U	Density (g/cc)			Surface Area (m^2/cc)			Roughness Factor (Sg/Sp)
			He	CCl_4	Bulk	BET (Sg)	Permeability Porosity (Sp)		
Ammonium hydroxide precipitated diuranate	32 hr at 850°-950°C	2.07	11.11±0.2	10.81	1.07	37.4	0.771	13.9	2.7
Urea precipitated diuranate	16 hr at 800°C	2.08	10.74±0.2	10.19	0.83	42.1	0.750	12.6	3.3
Ammonia precipitated diuranate	56 hr at 900°C	2.05	--	10.85	1.79	40.8	0.590	3.5	11.7
Ammonium carbonate precipitated diuranate	64 hr at 900°C	2.06	--	10.30	1.50	40.7	0.765	4.1	9.9
Uranium peroxide	4 hr at 900°C	2.08	11.00±0.1	10.78	1.34	28.4	0.651	9.8	2.9
Uranyl oxalate	64 hr at 900°C	2.01	10.61±0.2	10.61	1.07	7.3	0.780	5.0	1.5

10.79 to 11.16 as the O/U ratio increased from 2.00 to 2.25. In a recent study (Ref 21) using helium and CCl_4 as displacing media, it was found that uranium oxide samples with O/U ratios from 2.01-2.25, had measured densities which varied from 10.13-10.42. The density of a UO_2 preparation, therefore, depends upon its O/U ratio as well as on the density of its parent higher oxide.

Since the bulk density is a function of particle size distribution, porosity, and particle shape, the effects of preparation procedure on bulk density are complex and difficult to evaluate. The oxides prepared through the crystal growth and fluidized bed methods had the highest bulk densities (Table III). The powders prepared through precipitation procedures had the lowest bulk densities (Tables V and VI). The bulk density generally decreased with increasing fineness of the powder.

Surface Area Measurements

Surface area measurements obtained by gas adsorption techniques measure the total area of a solid. Porous bodies possess, in addition to their external (macroscopic) surface, an internal (microscopic) surface. Both external and internal areas are important characteristics in the performance of a powder. If sedimentation rates, resistance to flow of gases, bulk density, and packing problems are of concern, then the external area is the relevant quantity, but if rates of solution and oxidation or hygroscopic properties are of concern, then the total area is the required quantity (Ref 22). In addition, the number of points of contact between particles during sintering is a function of the external surface, while the role of surface impurities and adsorbed gases are functions of the total surface (Ref 19).

A permeability method also gives estimated measurements of the surface area of a solid. In this method, the velocity of a fluid under a constant pressure gradient through a packed bed of powder is measured. The porosity of the packed bed is a factor determining the rate of flow and must, therefore, be known. The method may give a good estimate of the total surface area of an ideal powder composed of non-porous particles of uniform size, shape, and packing. The surface area measured by the permeability method will be lower than that determined by gas adsorption to the extent that the powder does not conform to these ideal specifications (Refs 22 and 23). The adsorption method measures total accessible surface. The permeability method measures only surface available to flow. Surface area attributed to surface roughness and internal surface porosity are not

TABLE VI

PROPERTIES OF UO_2 PREPARED BY REDUCTION OF U_3O_8 OBTAINED FROM URANIUM PRECIPITATES

Method of Preparation	Reduction Conditions	O/U	Density (g/cc)			Surface Area (m^2/cc)			Roughness Factor (Sg/Sp)
			He	CCl_4	Bulk	BET (Sg)	Permeability Porosity (Sp)		
MCW UO_2 : pyrohydrolysis of ammonium hydroxide precipitated diuranate; reduction to UO_2	Reduced with cracked ammonia	2.02	10.75 $\pm$ 0.1	10.84	2.07	15.4	0.660	3.3	4.7
Air ignition (500°C) of ammonium hydroxide precipitated diuranate; hydrogen reduction to UO_2	34 hr at 800°C	2.14	11.09 $\pm$ 0.15	10.77	1.38	59.9	0.731	12.9	4.6
Air ignition (800°C) of ammonium hydroxide precipitated diuranate; hydrogen reduction to UO_2	25 hr at 900°C	2.02	10.61 $\pm$ 0.15	10.71	0.89	9.7	0.656	5.5	1.8
Air ignition (500°C) of urea precipitated diuranate; hydrogen reduction to UO_2	32 hr at 900°-1050°C	2.11	11.34 $\pm$ 0.2	10.47	1.00	60.4	0.768	10.3	5.9
Air ignition (800°C) of urea precipitated diuranate; hydrogen reduction to UO_2	40 hr at 900°C	2.01	10.55 $\pm$ 0.15	10.43	1.41	6.0	0.727	3.7	1.6
Air ignition (500°C) of ammonia precipitated diuranate; hydrogen reduction to UO_2	80 hr at 900°C	2.13	10.75 $\pm$ 0.15	10.82	1.50	58.0	0.654	16.8	3.4
Air ignition (500°C) of ammonium carbonate precipitated diuranate; hydrogen reduction to UO_2	110 hr at 900°C	2.05	--	10.30	1.61	36.2	0.766	3.9	9.3
Air ignition (1000°C) of ammonium carbonate precipitated diuranate; hydrogen reduction to UO_2	16 hr at 900°C	2.02	--	10.46	1.77	14.1	0.706	3.1	4.5
Air ignition (500°C) of uranium peroxide; hydrogen reduction to UO_2	56 hr at 900°C	2.02	--	10.44	1.91	11.9	0.650	3.2	3.7
Air ignition (500°C) of uranyl oxalate; hydrogen reduction to UO_2	62 hr at 900°C	2.03	--	10.68	0.98	30.4	0.788	6.6	4.6

measured (Ref 24). However, the ratio of the surface areas determined by the gas adsorption and permeability methods, termed the "roughness factor," may give some indication of the degree of porosity, irregularity, and non-uniformity of the powder particles. When this ratio is unity, a powder can be considered as non-porous. Thus, the relationship between gas adsorption and permeability measurements of surface area is similar to the relationship between measurements of density by helium and liquid displacement.

The total (BET) and external (permeability) surface areas for UO_2 powders prepared by steam oxidation procedures are listed in Table II. The surface areas are reported per unit volume of solid material rather than per unit mass in order to compare areas of powders with different densities. For the most part these UO_2 powders had relatively low total surface areas, which is reasonable, since the UO_2 preparations were made from uranium metal foil which itself has a low surface area. Since a fine powder is made by the decomposition of UH_3 , UO_2 prepared by steam oxidation of hydrided uranium had a much greater surface area than the oxides made by other steam oxidation methods. The total and external specific surface areas for the UO_2 prepared by the controlled low pressure steam oxidation technique were approximately equal. This is in agreement with the photomicrograph and density data which show that this oxide powder is composed of coarse, dense particles with no open porosity. For the other powders, the external surface areas were lower than the total surface areas, which is again consistent with the microscopic and density results in showing coarse, dense particles with varying amounts of open porosity.

As shown in Table III, hydrogen reduction of the higher uranium oxides usually resulted in UO_2 powders with relatively low total surface areas and roughness factors. The total surface areas and roughness factors of the UO_2 prepared by both fluidized bed denitration and UO_3 reduction were much higher than those of oxide made by fluidized bed denitration and standard hydrogen reduction of the UO_3 . This, in agreement with the microscopic and density data, indicates that the former powder is more porous and contains many more surface irregularities which the gas molecules can penetrate. The surface areas and roughness factors of UO_2 powders prepared by hydrogen reduction of U_3O_8 were very low. Only U_3O_8 made by ignition of finely powdered uranium from UH_3 gave a UO_2 powder with a higher specific surface area than Mallinckrodt oxide, and even then the value was less than half that of UO_2 prepared by steam oxidation of the same uranium powder. As will be discussed later, the 800°C temperature of preparation of the U_3O_8 may have contributed to the low specific surfaces. The low roughness factors (1.3-2.0) of these powders are consistent with their helium and liquid displacement densities in showing the presence of little or no open porosity.

In agreement with the results of Anderson, et al. (Ref 1), the data of Tables IV and VII show that the total surface areas of the UO_2 preparations made from UO_3 depend on the surface area of the UO_3 , rather than that of the original uranyl nitrate hexahydrate, and on the temperature of reduction. UO_3 powders with surface areas of 2.76 and $1.24 \text{ m}^2/\text{g}$ yielded under approximately the same reduction conditions (16 hr and 800°C) UO_2 preparations with surface areas of 1.33 and $0.63 \text{ m}^2/\text{g}$, respectively. The extremely low total surface ($0.05 \text{ m}^2/\text{g}$) of UO_2 prepared by the crystal growth method is probably caused by both the low surface area of the parent $\text{UO}_3 \cdot \text{H}_2\text{O}$ ($0.19 \text{ m}^2/\text{g}$) and the high temperature of reduction (1700°C).

The marked dependence of total surface area on the temperature of reduction is shown in Table VII and Fig. 14. Only at a reduction temperature of 480°C was the surface area of the UO_2 ($2.37 \text{ m}^2/\text{g}$) equivalent to that of the parent UO_3 ($2.76 \text{ m}^2/\text{g}$). In agreement with the microscopic observations (Fig. 6), both the total surface and the roughness factor decreased as the reduction temperature increased, indicating a considerable amount of particle growth and decrease of pores. Below 1650°C , the temperature of reduction did not seem to affect either the fluid or bulk density values. Those preparations with slightly greater densities had somewhat higher O/U ratios. At 1650°C , however, there was a noticeable increase in both fluid and bulk densities and the roughness

TABLE VII

EFFECT OF TEMPERATURE OF PREPARATION ON PHYSICAL PROPERTIES OF UO_2 POWDERS
 METHOD OF PREPARATION: HYDROGEN REDUCTION OF MILLED UO_3 ($2.76 \text{ m}^2/\text{g}$)
 REDUCTION TIME: 16 HR

Reduction Temperature (°C)	O/U	Density (g/cc)			Surface Area (m^2/cc)			Roughness Factor (Sg/Sp)
		He	CCl_4	Bulk	BET (Sg)	Permeability Porosity	(Sp)	
480	2.04	--	10.44	2.25	24.7	0.645	3.4	7.3
580	2.03	--	10.44	1.93	17.8	0.645	4.8	3.7
690	2.03	--	10.42	1.94	18.1	0.645	4.7	3.9
805	2.02	10.32 ± 0.1	10.36	2.03	13.8	0.654	4.0	3.5
920	2.02	--	10.39	2.00	13.2	0.645	3.5	3.8
1180	2.01	10.24 ± 0.05	10.28	1.84	9.4	0.645	3.6	2.6
1650	2.00	--	10.73	3.74	1.3	0.550	1.7	0.8

NOTE: The hydrogen atmosphere was also present during heating and cooling

factor decreased to approximately unity. Most of the closed pores were eliminated, and large-grained, non-porous UO_2 particles resulted. Anderson, et al. (Ref 1) also observed that heating low density UO_2 caused an increase in its density.

Total surface area and fluid density measurements were performed on the ammonium diuranate, uranium peroxide, uranyl oxalate, and U_3O_8 powders in an effort to ascertain any correlation between the properties of the precipitate, the intermediate U_3O_8 , and the resulting UO_2 . The results are given in Table IV. The ammonium diuranate prepared by precipitation with gaseous ammonia and ammonium hydroxide had the largest specific area, the lowest density, and on the basis of X-ray measurements, the smallest crystallite size. This is consistent with the fact that precipitation with these reagents occurs rapidly and forms a finely divided, poorly crystallized powder. Precipitation from urea and ammonium carbonate solution occurs slowly and yields a material of larger crystallite and particle size and smaller specific surface.

Although both of these diuranate powders were prepared by methods involving slow precipitation, microscopic examination showed that the ammonium-carbonate precipitated diuranate was composed of uniform spherical particles, whereas the diuranate particles obtained from urea solution were somewhat distributed in size and shape. This suggests that the former is a more carefully crystallized powder and contains fewer closed pores, a conclusion which is borne out by its greater density. The similarity in surface area may indicate that its average particle size is smaller than that of the urea precipitated diuranate.

Surface area measurements for UO_2 powders prepared by direct reduction of the uranium precipitates are given in Table V. The total surface areas and roughness factors were usually somewhat lower than those of the UO_2 powders prepared by first pyrolyzing the precipitates to U_3O_8 at 500°C and then reducing with hydrogen (Table VI). The high roughness factors (10 and 12) for the UO_2 powders prepared from ammonium carbonate and ammonia precipitated diuranate are consistent with their microscopic appearance which shows extremely porous particles. The low roughness factor (1.5) for the UO_2 obtained from uranyl oxalate agrees with the liquid and helium displacement density values in showing no open porosity. A roughness factor of approximately 3 was found for the remainder of these UO_2 preparations, which was consistent with the density measurements in indicating the presence of some open pores. As seen in Table IV, there is no apparent relationship between the specific surface area of the parent ammonium diuranates and the derivative UO_2 powders.

Although the urea and ammonium carbonate precipitated diuranates had approximately $2/5$ the area of the diuranates obtained by ammonia addition, the final UO_2 powders had almost equal surface areas.

As stated previously, the UO_2 powders prepared from ammonium diuranate by hydrogen reduction for 16 hr at $800\text{--}900^\circ\text{C}$ were pyrophoric and oxidized to a black material. This is in agreement with Anderson, et al. who obtained pyrophoric UO_2 by flowing hydrogen over UO_3 and ammonium diuranate contained in a boat in a tube furnace. They concluded that the reactivity of a UO_2 preparation, at least towards oxygen, is a function of particle size alone. The pyrophoric powders could be stabilized by using longer reduction periods and/or higher reduction temperatures. However, as shown in Table VIII, total surface area measurements on both the pyrophoric and stabilized powders gave rather similar values. These surprising results indicate that stabilization is not caused by particle growth. No explanation can be offered for this phenomenon.

TABLE VIII
EFFECT OF REDUCTION CONDITIONS ON THE STABILITY OF UO_2 POWDERS

Method of Preparation	Reduction Conditions	Oxide Stability	O/U	BET	Color
				Surface Area (m^2/g)	
Direct hydrogen reduction of ammonium hydroxide precipitated diuranate	16 hr at 900°C	pyrophoric	2.34	3.73	black
Direct hydrogen reduction of ammonium hydroxide precipitated diuranate	32 hr at 900°C	non-pyrophoric	2.07	3.37	brown
Air ignition of ammonium hydroxide precipitated diuranate to U_3O_8 ; hydrogen reduction to UO_2	17 hr at 800°C	pyrophoric	2.22	5.18	black
Air ignition of ammonium hydroxide precipitated diuranate to U_3O_8 ; hydrogen reduction to UO_2	34 hr at 800°C	non-pyrophoric	2.14	5.41	brown
Air ignition of urea precipitated diuranate to U_3O_8 ; hydrogen reduction to UO_2	16 hr at 900°C	pyrophoric	2.34	4.65	black
Air ignition of urea precipitated diuranate to U_3O_8 ; hydrogen reduction to UO_2	32 hr at $900^\circ\text{--}1050^\circ\text{C}$	non-pyrophoric	2.11	5.33	brown

Surface area values for the UO_2 powders prepared by reduction of U_3O_8 obtained from the uranium precipitates are listed in Table VI. The total surface areas for these powders were the highest of all UO_2 preparation surface areas studied, even though the temperatures of reduction were 900°C or higher in most cases. However, the UO_2 powders obtained by reduction of U_3O_8 , prepared by air ignition at $800\text{--}1000^\circ\text{C}$, had low total and external surface areas. The U_3O_8 ignition temperatures, therefore, are important in determining U_3O_8 and UO_2 product surface areas. The data of Table IV, again in agreement with the results of Anderson, et al., clearly show the dependence of the surface areas of these UO_2 preparations upon the surface areas of the parent U_3O_8 . As was found for the other UO_2 preparations, the roughness factors (4.5-6) in Table VI generally correlated with the density measurements in indicating varying amounts of open porosity. A high roughness factor (9.3) was again found for UO_2 prepared from ammonium carbonate precipitated

diuranate. However, the reason for the relatively high external surface area observed for the UO_2 obtained from ammonia precipitated diuranate is not known.

Mechanical and Thermal Treatments

The effects of various comminution treatments on the properties of uranium oxide powders are given in Table IX. * As would be expected, grinding appreciably increased both the total and external surface areas and decreased the bulk densities. This is in agreement with the microscopic evidence and particle size distribution analyses. (Refer to the following section of this report entitled: Particle Size Distribution Analyses.)

Grinding the UO_2 powders did not increase their densities significantly. The comminution processes, therefore, apparently did not open any of the closed pores. However, heating a UO_2 preparation at 1650°C increased the density from 10.27-10.71 g/cc. These results are in agreement with the work of Anderson, et al. Milling the less-abrasive UO_3 produced some increase in its density. The increase in density and surface area for ball-milled UO_3 was also retained upon reduction to UO_2 .

Adsorbed gases and vapors interfered with the measurement of the surface areas of UO_2 when the gas adsorption method was used. When the degassing temperature was increased from 100 to 400°C , the as-measured surface areas increased by 20%. Degassing above 700°C caused some decrease in the surface area values, probably because of sintering. A standard technique for degassing the samples at 400°C was therefore adopted. Surface area and density measurements, performed on a sample of $\text{UO}_{2.00}$ made by reduction of Mallinckrodt PWR Core I $\text{UO}_{2.02}$ (prepared at 815°C), were very close to those of the original Mallinckrodt "as prepared" oxide (Table X). * This indicates that little sintering occurs in the Mallinckrodt powder when it is heated in hydrogen at 800°C . In another experiment, a sample of Mallinckrodt UO_2 was heated in vacuo (10^{-6} mm Hg) at 1000°C for 24 hr. Although the real density was only slightly increased by the treatment, the surface area was reduced to 1/3 its former value, suggesting that some sintering occurs which does not alter the amount of closed porosity. Anderson, et al. also observed that heating UO_2 powders above their temperature of preparation always increased their particle size.

Gas adsorption measurements on sieve fractions of Mallinckrodt PWR Core I UO_2 (Table X) indicated that the powders are similar in structure and that the large particles are agglomerates of small ones. This conclusion is consistent with that based on microscopic examination. Oxidation (at 200° , 230° , and 277°C) of UO_2 to $\text{UO}_{2.25}$ and $\text{UO}_{2.34}$ caused little change in the surface area, showing that oxidation did not cause significant particle breakdown. Inasmuch as the differences in density between UO_2 , U_4O_9 , and U_3O_7 (11.0, 11.3, and 11.4 g/cc, respectively, calculated from the measured lattice dimensions) are small, these results appear reasonable. As was observed with the UO_2 powders, annealing above the temperature of preparation caused some particle growth. Further oxidation (300° and 326°C) to U_3O_8 caused a four-fold increase in surface area. Since conversion to U_3O_8 involves a considerable expansion, (a tetragonal unit cell of density 11.4 g/cc, changing to an orthorhombic cell of density 8.39 g/cc), it is likely that this large increase in volume strained the lattice and caused the large amount of particle breakdown observed. However, the surface area of U_3O_8 powder prepared by air oxidation of Mallinckrodt oxide at 800°C was half that of the starting material, and its real density was below theoretical. On the basis of these data, it appears that sintering occurs, but the closed porosity is retained on ignition of Mallinckrodt UO_2 to U_3O_8 in air at a temperature as low as 800°C . This agrees with previous investigations (Table IV) where it was found that air pyrolysis of the uranium precipitates (ammonium diuranate, uranium peroxide, and uranyl oxalate) to U_3O_8 at 500°C resulted in no change or, more often, an increase in

* Tables IX and X can be found on pp 18, 19, and 20.

specific surface area, whereas air ignition at 800°C or higher drastically decreased the surface area. Air ignition at the higher temperatures also caused an increase in density.

Surface area measurements performed on UO_2 powders that had been reduced from U_3O_8 at 700°, 600°, and 500°C gave values for the specific surface of 0.37, 0.40, and 0.64 m^2/g , respectively, as compared with a value of 0.33 m^2/g for the original U_3O_8 powder. An increasing amount of breakdown, therefore, occurs as the temperature of reduction is lowered. Greater particle breakdown probably occurs at the lower temperatures because mobility is lower in solids, and strains resulting from the phase transformation are less easily annealed out at the lower temperatures. The breakdown itself can be explained on the basis of the difference in crystal structure and density, (an orthorhombic unit cell of density 8.39 g/cc changing to a cubic cell of density 10.97 g/cc). No particle breakdown was observed when β -cubic U_4O_9 (0.46 and 0.73 m^2/g) and hexagonal UO_3 (2.77 m^2/g) samples were reduced at 410° and 480°C to UO_2 (0.45, 0.80, and 2.37 m^2/g), respectively.

Particle Size Distribution Analyses

Gas adsorption measurements give the total surface area of a powder. "Mean" or "average" particle diameters are usually calculated from such measurements on the assumption that the powder is composed of ideal uniform spheres. Particles in a real powder generally have a variety of sizes and shapes and differ in surface roughness and porosity. The calculated average particle diameters may in some cases have little physical meaning. The assumption of uniform spheres is also made in calculating average particle diameters from permeability measurements. The permeability measurement may, however, give a better indication of the physical size of the particles, since the internal surface area and the surface roughness of the particles are not measured by this technique.

Surface area and average particle diameters can also be calculated from a third type of measurement—by sedimentation and elutriation techniques which are used basically for measuring particle size distributions. One might expect reasonable agreement between the surface areas and the average particle diameters calculated from permeability measurements and from particle size distribution measurements, since in both cases the geometric sizes of the particles are of primary importance. However, as shown in the following, average particle diameters calculated from particle size distribution measurements are generally severalfold greater than those calculated from permeability measurements. The difference can be attributed to the fact that most powders are agglomerated, i. e., they are composed of aggregates of more or less loosely bound discrete particles. However, the three experimental techniques together give much complementary information on the size, shape, degree of porosity, and degree of aggregation of powder particles.

The particle size distribution curves, (a particle size determined by air sedimentation) for several representative UO_2 powders are plotted in Fig. 15. All the powders have a wide range of particle size, varying generally from 5-50 microns. Although an "average" particle diameter of about 2 microns is obtained from permeability measurements for these UO_2 powders, their particle size distributions differ appreciably. The large particle size of the UO_2 prepared by spray denitration and fluidized bed reduction is consistent with microscopic, density, and roughness factor data in indicating that this powder is composed of highly porous particles.

The effect of the ammonium diuranate precipitant on the particle size distribution of UO_2 powders is given in Fig. 16. The particle size analyses are in agreement with the microscopic evidence. The UO_2 particles prepared from ammonium hydroxide and ammonia-precipitated diuranate varied widely in size; urea-precipitated diuranate yielded oxide with less particle size variation, whereas UO_2 made from ammonium diuranate precipitated with ammonium carbonate had a relatively narrow size range.

The size distributions of Mallinckrodt uranyl nitrate hexahydrate, UO_3 , and UO_2 , plotted in Fig. 17, show that the particle size range of Mallinckrodt UO_2 is much closer to that of the parent

TABLE IX
EFFECT OF BALL-MILLING ON THE PHYSICAL PROPERTIES OF UO_2 POWDER

Type of Oxide	Milling Conditions	O/U	Density (g/cc)			Surface Area (m^2/cc)				Roughness Factor (Sg/Sp)
			He	CCl_4	Bulk	BET (Sg)	Permeability Porosity	(Sp)	Micromerograph	
MCW PWR Core I UO_2	As-prepared	2.02	10.16±0.05	10.15	2.77	6.4	0.645	3.1	0.9	2.0
MCW PWR Core I UO_2	Wet-milled, 860-g U slugs; 16-hr milling time	2.02	--	10.23	1.58	18.3	0.648	5.6	2.9	3.3
MCW PWR Core I UO_2	Wet-milled, 860-g U slugs; 40-hr milling time	2.05	--	10.22	1.64	17.5	0.662	6.6	3.0	2.7
MCW PWR Core I UO_2	Wet-milled, 1500-g U balls; 16-hr milling time	2.04	--	10.32	1.88	31.5	0.647	6.1	3.6	5.2
MCW PWR Core I UO_2	Wet-milled, 2000-g Zircaloy-2 balls; 16-hr milling time	2.10	10.28±0.1	10.26	2.16	53.1	0.534	17.1	--	3.1
MCW PWR Core I UO_2	Micronized: fluid jet grinding	2.04	--	10.22	1.66	19.7	0.640	6.8	3.7	2.9
MCW PWR Core I UO_2	Microatomized: high speed hammer milling	2.04	--	10.19	--	14.2	0.660	9.2	--	1.5
Hydrogen-reduced UO_3 from $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	--	2.02	9.96±0.1	10.02	2.16	5.4	0.650	3.1	--	1.7
Hydrogen-reduced dry milled UO_3	800-g UO_3 ; 2000-g Zircaloy-2 balls; 16-hr milling time	2.02	10.32±0.1	10.36	2.03	13.8	0.645	4.0	1.3	3.5
Hydrogen-reduced dry milled UO_3	Dry-milled, 860-g U slugs; 16-hr milling time	2.03	--	10.34	1.98	25.6	0.610	6.1	3.6	4.2

Hydrogen-reduced dry milled UO_3	Wet-milled, 860-g U slugs, 16-hr milling time	2.02	--	10.27	2.02	27.5	0.610	8.0	3.9	3.4
Hydrogen-reduced dry milled UO_3 , annealed in hydrogen at 1650°C for 21 hr	Wet-milled, 860-g U slugs, 16-hr milling time	2.00	--	10.71	--	13.9	--	--	--	--
Hydrogen-reduced wet milled UO_3	1700 ml of 0.02N H_2SO_4 , 700-g UO_3 , 1100-g Zircaloy-2 balls, 4-hr milling time	2.03	10.68±0.1	10.32	1.22	17.5	0.763	7.7	--	2.3
MCW UO_2 from ammonium diuranate	As-prepared	2.02	10.75±0.1	10.84	2.07	15.4	0.660	3.3	0.8	4.7
MCW UO_2 from ammonium diuranate	Wet-milled, 860-g U slugs, 16-hr milling time	2.05	--	10.79	1.93	24.2	0.664	6.7	3.8	3.6
UO_2 from urea precipitated diuranate	As-prepared	2.02	--	10.53	2.22	17.0	0.773	4.3	1.2	4.0
UO_2 from urea precipitated diuranate	Wet-milled, 860-g U slugs, 16-hr milling time	2.05	--	10.52	1.90	29.9	0.675	5.7	3.5	5.2

NOTE. The UO_3 powders were milled in Zircaloy-2 containers. The UO_2 powders were milled in rubber-lined cylinders, the wet-milling conditions were 64 ml H_2O 200 g UO_2 .

TABLE X
EFFECT OF VARIOUS THERMAL TREATMENTS ON THE
PHYSICAL PROPERTIES OF UO_2 POWDERS

UO_2 Thermal Treatment	O/U	Displacing Fluid	Density (g/cc)	Total Surface Area (m^2/g)
MCW PWR "as-prepared" UO_2	2.02	Helium	10.15 ± 0.05	0.61
-325 mesh MCW oxide	2.02	Helium	10.19 ± 0.05	0.62
+325 mesh MCW oxide	2.02	Helium	10.27 ± 0.05	0.62
MCW oxide heated in vacuo 1 hr at 700°C	2.02	--	--	0.56
MCW oxide heated in vacuo 1 hr at 800°C	2.02	--	--	0.53
Microatomized MCW UO_2	2.04	CCl_4	10.19	1.39
Microatomized MCW UO_2 heated in vacuo 1 hr at 730°C	2.04	--	--	1.07
MCW oxide heated in hydrogen 20 hr at 800°C	2.00	CCl_4	10.15 ± 0.05	0.61
MCW oxide heated in vacuo 24 hr at 1000°C	2.02	Helium	10.28 ± 0.05	0.21
UO_3 -reduced UO_2 ($2.37 \text{ m}^2/\text{g}$) ignited in air at 200°C ; annealed two weeks at 200°C in vacuo	2.25	--	--	2.13
UO_3 -reduced UO_2 ($2.37 \text{ m}^2/\text{g}$) ignited in air at 200°C ; annealed in vacuo 1 week at 700°C	2.25	CCl_4	10.85	0.73
MCW UO_2 ignited in air at 200°C ; annealed in vacuo for one week at 800°C	2.25	CCl_4	10.34	0.53
MCW UO_2 ignited in air at 230°C	2.34	--	--	0.61
MCW UO_2 ignited in air at 277°C	2.35	--	--	0.72
MCW UO_2 ignited in air at 300°C	2.66	--	--	2.8
MCW UO_2 ignited in air at 326°C	2.66	--	--	2.4
MCW UO_2 ignited in air 6-12 hr at 800°C	2.66	Helium	7.91 ± 0.1	0.32

UO_3 than to that of the starting uranyl-nitrate hexahydrate. This indicates, as with surface area and density, that the particle size distribution of a UO_2 preparation is dependent (disregarding reduction temperature variation) upon that of the higher oxide from which it has been prepared by reduction. The effect of the temperature of reduction on the particle size distribution of UO_2 prepared from UO_3 is shown in Fig. 18. In agreement with microscopic and specific surface area measurements, a considerable amount of particle growth was observed as the reduction temperature increased. Only at a reduction temperature of 480°C was the particle size distribution of the UO_2 similar to that of the parent UO_3 .

The effect of different comminution procedures on the particle size distribution of UO_2 is shown in Figs. 19-21. Although the as-prepared powders differed appreciably in particle size distribution, the milled powders are rather similar (Fig. 19). The influence of wet- and dry-milling (Fig. 20), amount and type of grinding media (balls, slugs, rods, etc.), milling time, and comminution processes (Fig. 21) were studied. Little difference in the particle size distribution curves of the milled

powders was observed. In all cases the original UO_2 agglomerates were reduced to a 1-5 micron size range. Since the size ranges of the milled powders are relatively narrow, fair agreement might be expected between specific surface areas and "average" particle diameters for the same powder obtained from permeability and particle size distribution data. However, the "average" permeability particle diameter for the milled oxides is about one micron, and the permeability surface areas are generally double those calculated from the particle size distribution (Table IX). This indicates that even the milled powders exist in an agglomerated form. The electron micrograph shown in Fig. 22 supports this conclusion. The surface area calculated from the particle size distribution curve is, therefore, a measure of the external surface of these UO_2 agglomerates.

Studies were made of the effect of oxidation or reduction on the particle size distribution of the uranium oxides and the oxidation or reduction relationship with total surface area as determined by gas adsorption. A decrease occurred in both particle size and BET surface area when Mallinckrodt PWR Core I UO_2 and ammonium-carbonate precipitated diuranate were oxidized to U_3O_8 at 800 and 1000°C. Thus, while some sintering occurs at these temperatures to give a lower total surface area, the oxidation process tends to break up the agglomerates. No change in particle size distribution, but an increase in surface area, was observed on low temperature reduction (500°C) of U_3O_8 to UO_2 . Particle breakdown occurred and gave an increased total surface area, but the integrity of the agglomerates was retained. Finally, there was no change in either particle size distribution or surface area on low temperature reduction (410°C) of U_4O_9 to UO_2 . In this case, neither particle nor agglomerate breakdown occurred. This appears reasonable since there are no large changes in either crystal structure or density with the reduction of U_4O_9 to UO_2 .

Thermal Analyses

Thermogravimetric and differential thermal analysis (DTA) data have been found useful in characterizing UO_2 as to oxidation resistance, in detecting higher oxides, in calculating O/U ratios, and in estimating the amount of adsorbed water. Thermogravimetric and DTA curves were obtained for Mallinckrodt PWR Core I oxide, for UO_2 prepared by hydrogen reduction of milled UO_3 , for ammonium diuranate precipitation, and for steam oxidation. The results were in substantial agreement with ORNL studies (Ref 2).

In all cases, a weight loss caused by the evolution of water occurred around 100°C. The amount of adsorbed water and the initial O/U ratios calculated from thermal measurements were in fair agreement with the values obtained by chemical analyses. On heating in air, both the DTA and weight change curves indicated two exothermic reactions, $\text{UO}_2 \rightarrow \text{UO}_{2+x} \rightarrow \text{U}_3\text{O}_8$. The intermediate oxide was produced in the temperature range of 300-350°C and had an O/U ratio of 2.32-2.37, corresponding to U_3O_7 . The stability range of U_3O_8 occurred between 400-600°C and varied with the type of UO_2 . As the temperature was raised above 600°C, the U_3O_8 began to lose oxygen gradually, reaching an O/U ratio of 2.55 at 1400°C. On cooling, there was a gradual increase in weight and the oxide reverted to U_3O_8 .

Storage Stability

It has been reported (Ref 25) that UO_2 has a tendency to pick up both water and oxygen on standing. The amount is a function of its mode of preparation and atmospheric conditions during exposure. Therefore, studies were made of the storage stability of representative UO_2 samples prepared by different methods. Fifty-gram samples were placed in 10-cm petri dishes and uniformly exposed to air in a drying oven at $30 \pm 2^\circ\text{C}$ for one month. In agreement with Anderson, et al., some correlation was observed between the total surface area and storage stability of the UO_2 powders. The powders with the higher total surface areas ($15\text{-}60 \text{ m}^2/\text{cc}$) were susceptible to oxidation on storage. The low surface area oxides ($0.5\text{-}10 \text{ m}^2/\text{cc}$) were relatively stable. For the experimental conditions employed, the amount of water pickup was rather low in all cases (0.01-0.05%).

SUMMARY

The results of the Anderson, et al., studies concerning the dependence of UO_2 properties upon their mode of preparation are confirmed and their conclusions extended to UO_2 powders made by a large variety of oxidation and reduction methods. Although physical properties such as particle size and distribution, microstructure, porosity, crystallite size, surface area, and density can vary over a wide range, these properties can be controlled through the judicious choice of variables in the preparation procedure.

In a first approximation, the crystallite size of UO_2 powders depends more on the temperature than on the method of preparation. Low temperature preparations (350°C) produced the smallest crystallite sizes (200 Å); the crystallite size of UO_2 made at 800°C was considerably larger (1000 Å).

The real density of a UO_2 preparation depends upon its O/U ratio and on the density of its parent higher oxide. The density was not dependent on the reduction temperature up to 1200°C . However, heating low density UO_2 above its temperature of preparation can cause an increase in its density. In many cases the liquid displacement densities were considerably below the helium displacement values, indicating measurable amounts of open porosity. Grinding the UO_2 powders did not increase their densities (as determined by liquid or helium displacement) significantly, but did decrease their bulk densities. Milling the less abrasive UO_3 produced some increase in its density which was retained upon reduction to UO_2 .

There is no correlation between density and total BET surface area; a high surface area can be associated with either a high or a low density; a low surface area powder can have either a low or a high density. There appears to be no relationship between the density and total surface area of the parent ammonium diuranate precipitates and the derivative UO_2 powders.

Grinding UO_3 and UO_2 powders increased the surface area and decreased the particle size. The increase in surface area for ball-milled UO_3 was retained upon reduction to UO_2 . The influence of oxide source, wet- and dry-milling, amount and type of grinding media, milling time, and comminution processes on the particle size distribution of UO_2 was studied and little difference in the particle size distribution of the milled powders was observed.

The particle size distribution and total BET surface area of a UO_2 preparation depend upon the particle size distribution and surface area of the higher oxide from which it has been prepared by reduction and on the reduction temperature itself. In the reduction of UO_3 , the uranium dioxide reduction product was most similar in surface area and particle size distribution to the parent oxide at low temperatures (480°C). Particle growth occurred at higher temperatures. No change in particle size distribution but an increase in surface area was observed on low temperature reduction (500°C) of U_3O_8 to UO_2 . There was less particle breakdown at higher reduction temperatures. This suggests that the UO_2 particles are fractured U_3O_8 particles whose strains anneal out at higher temperatures.

APPENDIX I: PREPARATION OF URANIUM DIOXIDE POWDERS

High Pressure Steam Oxidation

Twenty-mil uranium metal foil pieces were inserted in platinum-lined metal capsules with 1/16-in. holes drilled in their caps. The capsules were then placed in autoclaves so that the holes in the caps were above the water level at all times. The autoclaves were degassed and heated to 343°C at 2200 psig for various periods of time. The O/U ratios were almost always less than 2.00 (1.85-1.99) for oxidation periods of from 6-72 hr. Attempts to detect the presence of unreacted uranium by noting any hydrogen liberated by the action of concentrated HCl on the oxide powder were unsuccessful. The as-prepared oxide tended to retain the physical shape of the original uranium metal foil but readily crumbled into a fine, dull black powder.

Low Pressure Steam Oxidation

Oxidation of uranium foil with flowing steam at pressures between 3.5-7.5 psig and temperatures between 150-450°C produced a powder having an O/U ratio greater than 2.00 (2.01-2.20). It was found that the heat of oxidation was so great that under certain conditions (large sample size, high steam rate, high temperature) the reaction "ran away," and the temperature of the uranium rose to as much as 250°C above the steam temperature. The larger the sample size, the lower the steam temperature needed to cause this action. The oxide was similar to the high pressure material in appearance. When the oxidation rate was controlled by limiting the steam flowrate and temperature, a highly lustrous crystalline powder was obtained.

In contrast to the high pressure preparations, considerable amounts of U(VI) were found in both "controlled" and "uncontrolled" low pressure powders. In the high pressure method, the hydrogen formed in the reaction is retained as a reducing atmosphere and retards oxidation to U(VI). In the low pressure procedure, however, the flowing steam carries the hydrogen formed out of the reaction chamber, and oxidation to U(VI) by any oxygen present could occur. Heating high pressure and both controlled and uncontrolled low pressure oxides in hydrogen at 800°C caused their colors to change from black to brown.

Reduction from UO_3 (Fig. 23)

Mallinckrodt Oxide

The Mallinckrodt Chemical Works prepares natural UO_2 as a by-product in the process of converting uranium ore into uranium metal ingots. Molten uranyl nitrate hexahydrate (UNH) is pyrolyzed to UO_3 in gas-fired stainless steel ignition vessels. The powdered UO_3 is reduced to UO_2 with cracked ammonia in a continuous process for 4 hr at 815°C.

Laboratory Preparation

Uranyl nitrate hexahydrate was converted to UO_3 in electrically heated (200-400°C) porcelain ware. The coarse UO_3 was milled for 16 hr in a Zircaloy-2 ball mill. (Several hundred ppm of zirconium were detected in the oxide powder by spectrographic analysis. The UO_3 (-200 mesh) was placed in platinum boats and reduced with dry hydrogen (0.1-0.2 l/hr-g) to a brown UO_2 . The hydrogen was dried by passing it through a liquid nitrogen trap. The hydrogen reduction temperatures were varied from 480-1650°C.

Spray Denitration Method

Molten uranyl nitrate hexahydrate was fed through a spray nozzle into a heated (approximately 350°C) fluidized bed of UO_3 (see Ref 2). By this process the uranyl nitrate solution was evaporated and thermally decomposed into spherical UO_3 particles. Reduction to UO_2 was carried out by passing a mixture of three parts hydrogen and one part nitrogen by volume upward through a bed of UO_3 at sufficient flowrate (about 0.3 fps) to cause the bed to fluidize. The temperature of the oxide bed was maintained at 700°C.

Reduction from $\text{UO}_3 \cdot 2 \text{H}_2\text{O}$ (Fig. 23)

Uranium trioxide dihydrate was prepared by mixing UO_3 with the theoretical amount of water and casting the slurry in a tray. The material set quickly at room temperature in a firm cake which was reduced at 850°C with hydrogen to form UO_2 in one piece.

Reduction from $\text{UO}_3 \cdot \text{H}_2\text{O}$ (Ref 2) (Fig. 23)

$\text{UO}_3 \cdot \text{H}_2\text{O}$ crystals were grown hydrothermally from a uranium peroxide-uranyl nitrate slurry at 250°C (700 psig) in an autoclave. The UO_3 hydrate was then heated for 1 hr at 450°C to drive off the water. The brick-red (probably anhydrous UO_3) product was reduced to UO_2 with hydrogen at 1700°C for 2 hr.

Reduction from U₃O₈ (Fig. 23)

Uranium metal foil pieces, UO₃ and UO₂ prepared by high pressure steam oxidation and hydrogen reduction (MCW) procedures, were ignited to U₃O₈ in air at 800°C. The U₃O₈ powders were then reduced at 800°C for 16 hr with hydrogen to form UO₂.

Uranium Hydride Method (Fig. 24)

Uranium metal foil was reacted with hydrogen at temperatures ranging from 150-200°C. The UH₃ was decomposed by heating in vacuo at 300-350°C (Ref 26). The resulting finely powdered uranium was steam oxidized for 5 hr at 5 psig and 400°C. The UO₂ was then treated with hydrogen at 750-850°C for 15 hr. In another procedure, the uranium powder was ignited to form U₃O₈ at 740°C and reduced with hydrogen for 16 hr at 800°C to form UO₂.

The Precipitation of Uranium Salts

Ammonium Diuranate

Ammonium diuranate, (NH₄)₂·U₂O₇, was precipitated from uranyl nitrate solution (50-250 g UNH/1) by the addition of ammonium hydroxide, gaseous ammonia, urea, and ammonium carbonate. Precipitation with ammonium hydroxide was studied in detail. Variables such as pH, concentration, temperature, rate and manner of precipitation, and digestion periods were carefully controlled. In spite of wide variations in precipitating conditions (Table XI), microscopic examination of the crystals produced by reaction with ammonium hydroxide showed a wide range of irregular shapes and sizes (1-600 microns) in every case.

Uniform spherical particles of ammonium diuranate were obtained by ammonium carbonate precipitation at a pH of 3. Very fine, minute ammonium diuranate particles were obtained by

TABLE XI

PRECIPITATION OF AMMONIUM DIURANATE UNDER VARIOUS CONDITIONS

Method of Precipitation	Precipitation Temperature (°C)	pH	Digestion Time	Digestion Temperature (°C)
1:1 NH ₄ OH to excess uranyl nitrate	25	8	none	none
Uranyl nitrate to excess NH ₄ OH	25	8	none	none
1:1 NH ₄ OH to uranyl nitrate	25	8	20 min	80
1:1 NH ₄ OH to uranyl nitrate	65	8	20 min	80
Concentrated solution*	25	8	15 min	100
Concentrated solution	25	8	24 hr	100
Concentrated solution	80	8	15 min	100
Extreme dilution**	25	8	15 min	100
Extreme dilution	100	8	15 min	100

* Precipitation at "concentrated solution" was carried out as follows: Concentrated solutions were mixed together; the suspension was digested with a large quantity of water to promote recrystallization and then filtered.

** Precipitation at "extreme dilution" was carried out as follows: The ammonium hydroxide and uranyl nitrate solutions were, with efficient stirring, slowly and simultaneously added from two burettes to a large volume (2.5-1) of water. The speed of addition of both reagents was regulated, so that there was never a large excess of either solution until the precipitation was complete.

bubbling gaseous ammonia through a fitted glass disc dispersion tube into a uranyl nitrate solution. The uranyl nitrate-urea solutions were boiled for 2 hr to hydrolyze the urea. The decomposition of the urea resulted in the homogeneous generation of ammonium hydroxide from within the solution. The pH of precipitation of the ammonium diuranate was 6.5.

The ammonium diuranate samples were washed with distilled water and then dried in vacuo (100 microns) at 70-100°C. The preparation conditions of the uranium precipitates and their conversion to UO_2 are outlined in Fig. 25.

Uranium Peroxide

Uranium peroxide, $\text{UO}_4 \cdot 2 \text{H}_2\text{O}$, was precipitated from hot (90°C) uranyl nitrate solution (250 g UNH/1) by the slow addition of 10% hydrogen peroxide. The pH of precipitation was 1.5. The precipitate was digested for 1 hr at 90°C, filtered, washed with distilled water, and dried in vacuo (100 microns) at 100°C.

Uranyl Oxalate

Uranyl oxalate, $\text{UO}_2(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$, was precipitated from hot (90°C) uranyl nitrate solution (250 g UNH/1) by the slow addition of 10% oxalic acid. The pH of precipitation was 2. The precipitate was digested for 1 hr at 90°C, filtered, washed with distilled water, and dried in vacuo (100 microns) at 100°C.

The Conversion of Uranium Salts to UO_2

Each of the precipitated uranium compounds, $(\text{NH}_4)_2 \text{U}_2\text{O}_7$, $\text{UO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{UO}_2(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$, was converted into UO_2 either directly by heating in hydrogen at 800-1000°C, or by first pyrolyzing the powders in air at 500-1000°C to form U_3O_8 and then reducing with hydrogen. The powders were placed in platinum boats and reduced with dry hydrogen (0.1-0.2 liter/hr-g) in tube furnaces. The hydrogen was dried by passing it through a liquid nitrogen trap.

Mallinckrodt Oxide (Ref 27)

MCW prepares enriched UO_2 on a commercial basis by a precipitation process. The raw material is liquified uranium hexafluoride. The UF_6 is hydrolyzed into hydrofluoric acid and uranyl fluoride. Ammonium diuranate is precipitated by adding aqueous ammonia (25-30%) to the uranyl fluoride solution. The ammonium diuranate is filtered, washed, dried, and pyrolyzed to form U_3O_8 . The U_3O_8 is reduced to UO_2 with cracked ammonia at 815°C.

APPENDIX II: A POLAROGRAPHIC METHOD FOR THE DETERMINATION OF URANIUM (VI) IN URANIUM DIOXIDE*

The following method is a modification of a polarographic method originally described by G. H. Tishkoff (Ref 6). Tishkoff's method depends upon the solubility of U(VI) in 0.1N hydrochloric acid.

Theory

Uranium (VI) exhibits satisfactory polarographic reduction waves in a variety of supporting electrolytes. A polarogram of U(VI) in a mixture of phosphoric and sulfuric acids shows a half-wave potential of about -0.05 v, measured against a saturated calomel electrode.

The method for polarographic analysis of U(VI) reported by Tishkoff was tried in this laboratory. The recovery of U(VI) from a sample of Mallinckrodt NY-ST U_3O_8 , determined in triplicate with 2N hydrochloric acid as a solvent; ranged from 42-47% of the theoretical value. The same sample, with 85% phosphoric acid as a solvent, yielded 96-102% recoveries of U(VI). Apparently the bulk of

* From work by R. M. Burd and G. W. Goward, Bettis Plant

U(VI) does not dissolve in hydrochloric acid because the U(IV) oxide is itself insoluble. The possibility exists then that a majority of the U(VI) oxide is entrapped in the U(IV) oxide.

Eighty-five percent phosphoric acid dissolves completely the entire portion of U(IV) oxide, thus assuring the analyst that all U(VI) will be dissolved; 4N sulfuric acid is used to dilute the mixture of U(IV) and U(VI) phosphate to a convenient volume.

By taking a 0.5 g sample of U(IV) oxide, it is possible to detect with this method as little as 0.1% of U(VI).

Reagents

- 1) Standard U(VI) solution. A satisfactory standard may be prepared from any high purity Mallinckrodt NY-ST U_3O_8 . U_3O_8 with a purity of 99.85% was used. Thus, 2.362 g of NY-ST U_3O_8 were dissolved in a small quantity of 1 to 1 nitric acid. The solution was fumed several times with small portions of 1 to 1 sulfuric acid and allowed to cool. After 2-3 ml of concentrated sulfuric acid was added, the solution was diluted with water to make 1-liter. One ml of this solution contained 2.0 mg U(VI).
- 2) Phosphoric acid, 85%
- 3) 4N sulfuric acid
- 4) Nitrogen

Procedure—Calibration Curve

- 1) Transfer 2, 4, 6, 8, and 10 ml of the master uranium standard [1 ml = 2 mg U(VI)] to 50-ml volumetric flasks.
- 2) Add 5 ml of 85% phosphoric acid, and dilute to the mark with 4N sulfuric acid. Mix well.
- 3) De-oxygenate each standard for approximately 20 min in a stream of nitrogen.
- 4) Record the polarogram at $25 \pm 0.050^\circ C$, reading the diffusion current at 0.5 v.
- 5) Determine the residual current of the electrolyte at -0.5 v, after de-oxygenating for 20 min.
- 6) After correcting the diffusion current by subtracting the residual current, construct a curve of diffusion current plotted against concentration of U(VI) in mg.

Procedure—U(IV) Oxide Samples

- 1) Weigh 0.1-0.5 g of powdered U(IV) oxide into a 100-ml Berzelius beaker.
- 2) Add 5 ml of 85% phosphoric acid.
- 3) Boil 5-10 min (or until solution is complete) in a nitrogen atmosphere.
- 4) Allow the solution to cool almost to room temperature, then add 45 ml of 4N sulfuric acid.
- 5) Place the beaker in a thermostatic water jacket or bath and allow the temperature to reach equilibrium at $25 \pm 0.50^\circ C$, while admitting a stream of nitrogen.
- 6) Record the polarogram, reading the diffusion current at -0.5 v.
- 7) From the height of the diffusion current, which has been corrected for the residual current, calculate the amount of U(VI) present.

Discussion

Four N sulfuric acid is used to dilute the solution of U(IV) and U(VI) phosphates to volume, because U(IV) phosphate is insoluble in weakly acidic or neutral solutions. A gelatinous precipitate is formed which loses water on heating and becomes glassy.

Occasionally during addition of the 4N sulfuric acid, a milky precipitate is formed. This precipitate is readily dissolved by additional heating of the sample.

Temperatures other than 25°C may be used, provided that calibration curves and samples are all determined at the same temperature.

This method could conceivably be adapted to the analysis of any uranium salt soluble in phosphoric acid.

APPENDIX III PREPARATION TECHNIQUES FOR INTERNAL MICROSTRUCTURE STUDIES OF UO_2 POWDERS

When UO_2 powders or small pieces of UO_2 compacts are to be examined in cross section, they are mounted in one of several ways. Two plastics have been used for the purpose, the more satisfactory of which is Kelon. * This plastic as-received from the manufacturer is a mixture of monomer and polymer methacrylates, judging from the viscosity and the curing temperature. A catalyst is added to the Kelon, with thorough mixing, and the resulting mixture is then poured over the powder in a suitable mold. The mount is allowed to "set-up" at room temperature for approximately 6 hr. Then, curing is completed by heating at 157°C for 1 hr. The other material used for mounting is Araldite. † As-received from the manufacturer, it is a powder containing the catalyst. The powder is melted over the UO_2 , then cured at about 200°C for 1/2 hr. Araldite cures to a thermosetting plastic and is preferred when greater heat stability is desired. It is a better adhesive than Kelon. Kelon is more generally used, however, because it cures at a lower temperature. The finished product contains no bubbles (as Araldite does), and penetrates deeper into the UO_2 powder pores.

The molds employed are of three types. The most generally used is made from a glass cylinder. The finished mold is about 3/4-1 in. in diam, about 1-in. high, and is mounted on a glass plate with modeling clay used as a seal on the outside of the cylinder. The powder to be examined is placed in the bottom of the mold, and Kelon is poured over it. After curing, the mold is disassembled and the sample is pushed out of the cylinder. This can be done with finger force since Kelon shrinks slightly during curing. The sample is then ground to the desired level in the powder layer and polished. During the grinding stage, viewing with reflected light incident from an oblique angle is helpful and the depth of the powder layer is readily determined. After polishing, the sample is viewed in a microscope having vertical illumination.

The two other types of mounts are used when the powder sample is to be cathodic vacuum-etched. These are made from metal discs about 5/8 in. in diam and 3/16 in. high. The mount used with Araldite has four small dimples made with a ball-peen hammer on one face, the mount used with Kelon contains an undercut, circular groove. The plastics are used as described before, except that the molds are integral parts of the mounts. If necessary, the sample is rough ground on a belt grinder, then hand ground on 400 grit silicon carbide wet or dry paper. The sample is polished in one of two ways, either run down through diamond abrasives, or polished on a Forstman cloth using Linde B powder. Care must be exercised to avoid relief polishing.

The samples are either chemically etched or cathodic vacuum-etched. The chemical etches used are 1:1 water-nitric acid or 10% H_2SO_4 in 30% H_2O_2 . Cathodic vacuum-etching is used according to procedures previously published and described for metals (Ref 28).

T. R. Padden, Bettis Plant

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† Ciba Company, Inc., Kimberton, Pa.

APPENDIX IV: DENSITY MEASUREMENT OF UO_2 BY HELIUM AND LIQUID DISPLACEMENT

Helium Displacement

The volume of a weighed sample of material can be determined by gas pressure measurements with helium gas. The helium is purified by passing it through activated charcoal at liquid nitrogen temperatures. The volume of the gas system is first measured. The volume of the system with the sample placed in it is then measured. The difference between the two values represents the volume of the sample.

Procedure and Calculations

The apparatus used is represented schematically in Fig. 26. The volume of the system is obtained in the following manner:

- 1) Charge the system with helium gas, and measure the pressure with the mercury level at mark A.
- 2) Raise the mercury through calibrated bulb C to mark B, and again measure the pressure.
- 3) If the pressure and volume in the system are, respectively, p_2 and v_2 at mark B and p_1 and $(v_2 + C)$ at mark A, then

$$p_2 v_2 = p_1 (v_2 + C) ,$$

and

$$v_2 = \frac{p_1 C}{p_2 - p_1} .$$

- 4) Sample weights are generally 20-30 g (2-3 cc).
- 5) Samples are degassed at a maximum pressure of 10^{-5} mm Hg for 1 hr at 400°C .
- 6) After a sample has been placed in the system, 10 min are allowed for pressure equilibration before readings are taken.
- 7) Corrections are made for temperature variations that occur between readings.
- 8) Five sets of readings are taken on each sample.

Precision of Method

Values obtained on samples of the same material having volumes of 2 cc generally agree to $\pm 1\%$. The precision increases with increasing sample size.

Liquid Displacement

The volume of the density bulb to be used is measured with distilled water as the standard liquid. The volume of a weighed sample is determined from the difference between the bulb volume and the volume of CCl_4 used to fill the dead space.

Procedure

The apparatus used in the liquid displacement method is shown schematically in Fig. 27. The volume of the sample is determined in the following manner:

- 1) Weigh bulb, cap, and sample.
- 2) Bulb C is filled to $1/3$ its volume with CCl_4 and immersed in liquid nitrogen until the CCl_4 is frozen.
- 3) The apparatus is slowly evacuated through stopcocks A and B for 20 min.
- 4) The liquid nitrogen is removed, stopcocks A and B are closed, and the CCl_4 is allowed to reach room temperature.

- 5) Stopcocks A and B are opened to the atmosphere in order to fill density bulb D with CCl_4 .
- 6) Density bulb D is immersed in a constant temperature bath. After temperature equilibrium has been attained, the excess CCl_4 above a calibrated reference mark on the density bulb is removed with a medicine dropper.
- 7) Density bulb D is capped, dried, and weighed. The weight of CCl_4 is determined from the difference in the known weights of the bulb, cap, and sample, and thus, the volume of CCl_4 is readily obtainable.

Precision of Method

Values obtained on samples of the same material having volumes of 2 cc generally agree within $\pm 0.2\%$.

APPENDIX V: INNES METHOD FOR DETERMINATION OF SURFACE AREA

The Innes surface area method is essentially a one-point rapid BET procedure (Ref 11). The Innes method involves a constant slow flow of gas into the adsorbent section of the apparatus so that equilibrium pressure is approximated and the amount of gas adsorbed is proportional to time. Surface area is calculated from the time required for nitrogen to reach a relative pressure end point of 0.2, using nitrogen as the adsorbent at liquid nitrogen temperature. The Innes apparatus and procedure have been slightly modified for this application.

Procedure and Calculations

The apparatus used is shown in Fig. 28. Because of the nature of the compounds studied, it was necessary that the system be operated under high vacuum (10^{-5} mm Hg) when degassing the samples at temperatures up to 400°C for 1-4 hr. Although the original Innes sample holder was constructed of metal, a less cumbersome and more convenient glass sample bulb with a ball and socket joint attachment was substituted. The primary feature of the Innes apparatus is that a very low but constant gas flowrate is maintained in the adsorbent section of the apparatus, so that the amount of gas introduced can be determined after a time measurement when the pressure in the sample section of the apparatus approximates equilibrium pressure. This is done with a flow controller which operates to maintain a constant 3-psi pressure drop across the capillary. Commercial flow controllers were unsatisfactory for the low flowrates desired (7-10 cc/min); a differential flow controller, employing a Hoke needle valve regulated by a pressure diaphragm and a 3-lb spring, gave the proper flow control. A constant forepressure (6.0-6.5 psi) was maintained with a Moore pressure regulator. A Heise-Bourdon gage was used for the vacuum and gas flowrate measurements. The quantity of gas introduced was determined from a time measurement. The specific surface area was then calculated from the following equation (for an equilibrium relative pressure end point of 0.2):

$$S = K (r t_{0.2} - C_1) / W$$

where

- S = specific surface, m^2/g
- K* = correction factor, 3.68 cm^{-1}
- r = flowrate, cm^3/sec
- $t_{0.2}$ = time for the relative pressure to reach a value of 0.2, sec
- C_1 = dead space correction for standard temperature and pressure, cm^3
- W = sample weight, g

The revised equation of Bini and Maresh (Ref 29) was used to calculate the surface area dead space correction, C_1 .

* This is obtained from the relation, surface area = $3.68 V_{0.2}$ obtained from the Brunauer, Emmett, and Teller equation, using the value of $16.2 \text{ \AA}^2$ for the cross sectional area of the nitrogen molecule. $V_{0.2}$ is the volume, in ml at stp, sorbed at a relative pressure of 0.2.

Comparative data on UO_2 powders were obtained from the Innes and conventional BET volumetric apparatus and show good agreement between the two methods (see Table XII). The reproducibility on duplicate measurements was generally within $\pm 5\%$.

TABLE XII
COMPARATIVE UO_2 SURFACE AREA VALUES

Method of Preparation	Surface Area (m^2/g)	
	BET	Innes
Hydrogen reduction of UO_3	0.36	0.44
Hydrogen reduction of UO_3	0.63	0.62
Hydrogen reduction of $\text{UO}_4 \cdot 2\text{H}_2\text{O}$	2.58	2.52
Hydrogen reduction of UO_3	2.90	3.41
Hydrogen reduction of urea-precipitated diuranate	3.92	4.14
NBS TiO_2	10.40	10.50

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(A)

(B)

Fig. 1 Comparison of the Two Types of Structure of High-Pressure Steam Manufactured UO_2 ; 250X

(A) Controlled Oxidation

(B) Uncontrolled Oxidation

(C) Hydride-Steam Oxidation

Fig. 2 Microstructure Comparison between the Three Types of Low-Pressure Steam Manufactured UO_2 ; 250X

(A) Uranium Foil Source

(B) Uranium Power Source

Fig. 3 Effect of Form of Uranium Metal on Microstructure of UO_2 Powders Prepared by Reduction of U_3O_8 ; 250X

(A) +80 Sieve Fraction,
177 μ and Higher

(B) +325 Sieve Fraction, 44 to 53 μ

(C) -325 Sieve Fraction,
0 to 44 μ

Fig. 4 Mallinckrodt UO_2 Powder Fractions, PWR Core 1; 500X

(A) As Prepared MCW PWR Core 1 UO_2 ; 250X

(B) MCW UO_2 , Prepared by Ammonium Diuranate-Precipitation; 250X

(C) Wet Ball-Milled MCW UO_2 ; 500X

Fig. 5 Effect of Ball-Milling on Microstructure of Mallinckrodt UO_2

(A) 480°C

(B) 800°C

(C) 1650°C

Fig. 6 Effect of Reduction Temperature on Microstructure of UO_2 Prepared from Ball-Milled UO_3 ; 250X

(A) From Fluidized Bed Denitrated UO_3

(B) From $\text{UO}_3 \cdot \text{H}_2\text{O}$ Crystals

Fig. 7 Microstructure of UO_2 Powders Prepared by Reduction of the Higher Uranium Oxides; 250X

(A) From High-Pressure Steam Manufactured UO_2

(B) From Mallinckrodt PWR Core 1 UO_2

Fig. 8 Effect of Oxidizing UO_2 to U_3O_8 and Reconverting Back to UO_2 by Hydrogen Reduction; 250X

(A) Direct Diuranate Reduction to UO_2

(B) Diuranate Ignition to U_3O_8 , Reduction to UO_2

Fig. 9 UO_2 Prepared from NH_4OH -Precipitated Diuranate, 250X

(A) Direct Diuranate Reduction to UO_2

(B) Diuranate Ignition to U_3O_8 , Reduction to UO_2

Fig. 10 UO_2 Prepared from Urea-Precipitated Diuranate; 250X

(A) Diuranate Ignition
to U_3O_8

(B) Reduction of U_3O_8
to UO_2

(C) Direct Diuranate
Reduction to UO_2

Fig. 11 UO_2 Prepared from $(NH_4)_2CO_3$ -Precipitated Diuranate; 250X

(A) Diuranate Ignition
to U_3O_8

(B) Reduction of U_3O_8
to UO_2

(C) Direct Diuranate
Reduction to UO_2

Fig. 12 UO_2 Prepared from NH_3 -Precipitated Diuranate; 250X

(A) Uranyl Oxalate Ignition
to U_3O_8

(B) Reduction of U_3O_8
to UO_2

(C) Direct Uranyl Oxalate
Reduction to UO_2

Fig. 13 UO_2 Prepared from Uranyl Oxalate; 250X

Fig. 14 Surface Area as a Function of Reduction Temperature

Fig 16 UO_2 Particle Size Distribution
Effect of Precipitation

Fig 17 Particle Size Distribution

Fig. 18 Particle Size Distribution: Effect of Reduction Temperature

Fig. 19 Particle Size Distribution: Effect of Milling Procedure

Fig. 20 Particle Size Distribution: Effect of Milling Procedure

Fig. 21 Particle Size Distribution: Effect of Comminution Process

Fig. 22 Electron Micrograph of Wet Ball-Milled MCW UO_2 ; 6800X

Fig. 23 Preparation of UO_2 by the Hydrogen Reduction of Higher Oxides

Fig. 24 Preparation of UO_2 by the Hydride Method

Fig. 25 Preparation of UO_2 by Precipitation Methods

Fig. 26 Helium Density Apparatus

Fig. 27 CCl_4 Liquid Density Apparatus

Fig. 28 Innes Surface Area Apparatus