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EVALUATION OF FUSED UO_2

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EVALUATION OF FUSED UO_2

by

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April 1963

E. I. DU PONT DE NEMOURS & COMPANY
EXPLOSIVES DEPARTMENT - ATOMIC ENERGY DIVISION
TECHNICAL DIVISION - SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA

CONTRACT AT (07-2) - 1 WITH THE
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ABSTRACT

The density and purity of fused UO_2 from several suppliers was evaluated. Densities of large pieces varied widely, but variations in pycnometer and bulk densities of crushed UO_2 powder were small. Average oxygen-to-uranium ratios ranged from 1.94 to 2.14. Impurities visible as microscopic inclusions were U_4O_9, metallic uranium, UC, and UN_2. The chief trace metallic contaminants were aluminum, iron, and silicon. Hydrogen, nitrogen, carbon monoxide, and carbon dioxide were evolved during vacuum extraction.

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EVALUATION OF FUSED UO_2

INTRODUCTION

Fused UO_2 is a dense ceramic that is well adapted for fuel elements made by swaging or vibrational compaction. These mechanical fabrication methods are low in cost, but the bulk fuel densities obtainable are limited by the density of the feed material. Fused UO_2 has essentially the theoretical density, 10.97 g/cm^3, but it often contains impurities that may influence its behavior in reactors. The densities and impurities of fused UO_2 from several suppliers were measured in connection with the power reactor fuel development program of the Savannah River Laboratory.

SUMMARY

Fused UO_2 received at SRL was generally satisfactorily dense, but it was variable in appearance, oxygen-to-uranium ratio, and impurity content.

The densities of 1/4- to 1/2-inch chunks of fused UO_2 ranged from approximately 7 to 11 g/cm^3, but pycnometer densities of particles pulverized to pass a 20 mesh sieve* were more uniform, ranging from 10.80 to 11.02 g/cm^3.

The average oxygen-to-uranium ratios of the fourteen lots evaluated ranged from 1.94 to 2.14. Excess oxygen content ($O/U > 2.00$) was related to macro-appearance.

Microscopic inclusions found were U_4O_9, metallic uranium, UC, and UN_2. The inclusions were initially identified in selected samples by X-ray diffraction, but tarnishing and etching characteristics and microhardness were used to identify inclusions in most of the samples.

Amounts of the chief metallic impurities ranged up to 160 ppm aluminum, 440 ppm iron, and 200 ppm silicon. These impurities were not associated with specific inclusions.

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* A screen with 20 wires per inch and square openings 0.033 inch on a side.

The principal gases evolved by the UO_2 when it was heated in a vacuum were hydrogen, nitrogen, carbon monoxide, and carbon dioxide. The quantity of evolved gas increased as particle size decreased and was greater at an extraction temperature of 1300°C than at 1000°C. A maximum total gas evolution of one cc (STP) per gram of UO_2 was observed for one specimen of -325 mesh powder.

DISCUSSION

SOURCES OF UO_2

The UO_2 discussed in this report was fused either in air by the Norton Company, under inert gas by the Spencer Chemical Company, or in an unspecified atmosphere by the Nuclear Materials and Equipment Corporation (NUMEC).

Two small orders of UO_2 densified by hydrogen sintering (high-firing) were evaluated along with the fused UO_2 as possible alternatives for use in reactor fuel elements.

Suppliers of both fused and sintered UO_2 are listed in Appendix A. Information about the UO_2 shipments is given in Table I. Appendix B lists four additional types of nonfused UO_2 used for comparison with fused UO_2 in the density studies.

TABLE I

Identification of the UO_2 Shipments

Designation(a)	Type of Process	Quantity, lb	Date Received	U^{235} Content
Norton I	Fused in air(b)	400	4/58	Natural
II		16,800	1/59	Natural
III		5,200	7/61;4/62	Natural
Spencer I	Fused under inert atmosphere	100	6/59	Natural
II		2,000	1/60	Natural
III		4,000	10/60	Natural
IV		3,000	1/61	1.5%
V		200	6/61	5.0%
VI-A		1	5/61	Depleted
VI-B		1	5/61	Depleted
VI-C		1	5/61	Depleted
NUMEC I	Unspecified	20	2/61	Natural
Davison I	Sintered	20	1/61	Natural
MN I	Sintered	20	3/61	Natural

(a) The name refers to the supplier (see Appendix A); the Roman numerals differentiate among orders from a given supplier.

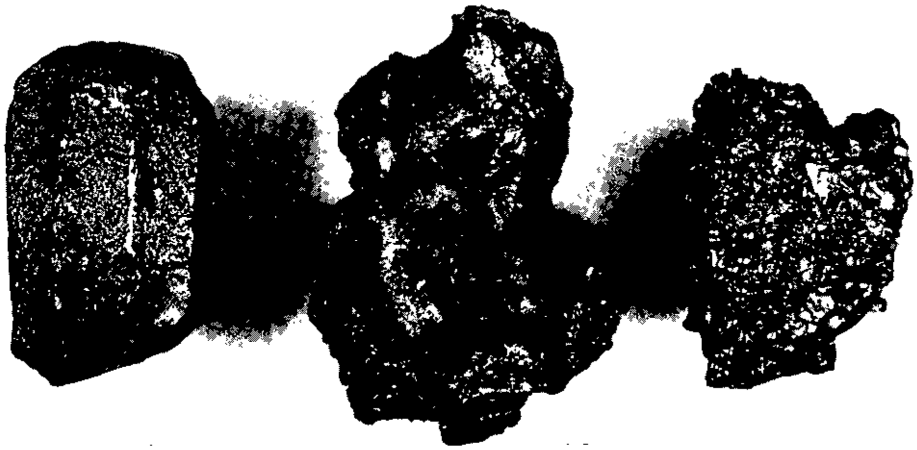
(b) The process was modified for the final 45 lots of the 54 lots making up the Norton III order to include final cooling under argon.

APPEARANCE OF FUSED UO_2

There were striking variations in appearance of the fused oxide received in the early Norton and Spencer orders, as shown in Figure 1. A system of classification based on appearance and designated by grade numbers was developed and applied to the Norton I and II orders. Examples of the graded UO_2 are shown in Figure 2; grades 3 and 4 are not pictured because they occurred only as chips or powder.

Neg. 21377 ~1X Neg. 21837 ~1X

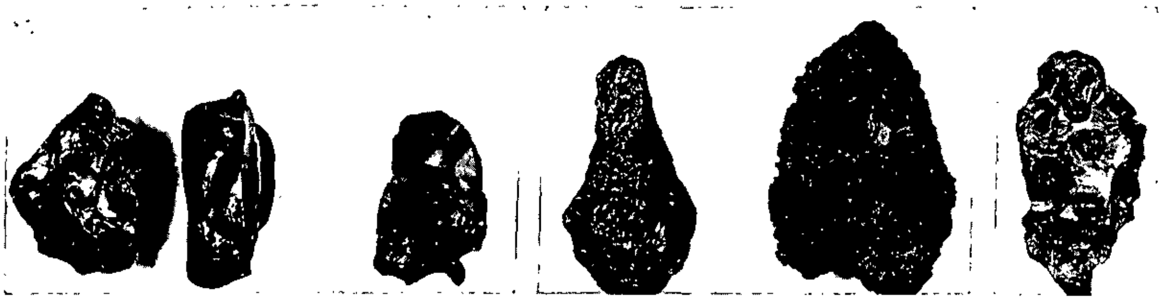
Norton II (Fused in Air)



Neg. 21378 ~3X

Spencer I (Fused in Protective Atmosphere)

FIG. 1 VARIATIONS IN APPEARANCE OF THE EARLY ORDERS OF FUSED UO_2



Grade Number	Description
1	Smooth and shiny, with good crystal faces
2+	Smooth, but with dull surfaces
2	Rough surfaces
2-	Rough, dull surfaces
3	Crushing fines (a mixture of the other grades)
4	Loose powder at the bottom of the shipping container of the first shipment received. This oxide was not fused, but was the sintered "fire-sand" from around the fused material.
5	Shiny, but with large craters

FIG. 2 REPRESENTATIVE PIECES OF GRADED FUSED UO_2
From Norton I and II, both fused in air

DENSITY

MERCURY DISPLACEMENT DENSITIES

The densities of 1/4- to 1/2-inch pieces of fused UO_2 measured by displacement of mercury ranged from 7.25 to 11.27 g/cm^3.

The densities of these pieces of fused UO_2 were compared with appearance, or grade. Only the smooth, shiny pieces designated grade 1 oxide gave consistently high densities, essentially the theoretical density of 10.97 g/cm^3. The densities of the other grades were not only lower but also varied more widely than the grade 1 material, as shown in Table II.

PYCNOMETER DENSITIES

The densities of the pulverized UO_2 (usually -20 mesh), measured by displacement of water or carbon tetrachloride with a pycnometer, closely approached the theoretical density of 10.97 g/cm^3. This uniformity of densities of pulverized UO_2 contrasted markedly with the scattered densities of the larger pieces. The internal porosity that made the larger pieces vary in density was eliminated by crushing.

Pycnometer densities are listed in Table II.

DENSITIES OF BULK PULVERIZED UO_2

The densities of bulk pulverized UO_2 were measured on three types of specimen preparations: poured, tapped, and swaged. The average densities of the fused UO_2 were 5.6 g/cm^3 for poured specimens, 6.9 g/cm^3 for tapped specimens, and 10.0 g/cm^3 for swaged specimens.

Poured specimens were prepared by pouring UO_2 (-20 mesh) through a funnel to fall a given height into a container of known volume. Tapped specimens were prepared by tapping UO_2 (-20 mesh) to a minimum height in a graduated cylinder. Density of both poured and tapped specimens was calculated from the measured volume and weight of the UO_2 in the respective containers. Swaged specimens were obtained by cutting sections from swaged UO_2 fuel elements with stainless steel or Zircaloy sheaths; density was measured by a modified loss-of-weight method. UO_2 for swaging was either ground to -20 mesh or to -6 or -10 mesh with particle size distribution favorable for vibrational compaction.*

The densities of poured, tapped, and swaged specimens are listed in Table II.

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* Vibrational compaction before swaging did not increase the final density of bulk specimens, but it did reduce the number of swaging passes required.

TABLE II

Density Measurements of UO_2

Unit: g/cm^3

Designation(a)	1/4-1/2 inch Pieces (by Hg displacement)		Small Particles (by pycnometer(b))	Bulk Specimens		
	Avg	Range		Poured	Tapped	Swaged(c)
Norton I						
Grade 1	10.96	10.87-11.05				10.1
2+	10.76	10.53-10.96				10.0
2	10.41	9.66-10.87				10.1
2-	8.90	7.25- 9.91				10.0
3	-					10.1
4	-					9.3
Norton II						
Grade 1	10.98	10.88-11.06	10.94	5.59	6.86	9.93
2+	10.72	9.95-11.27	10.94	-	-	9.94
2	10.44	9.87-10.72	10.98	5.70	6.78	10.00
2-	9.52	8.32-10.55	10.95	-	-	-
5	10.15	9.63-10.58	10.95	-	-	9.89
Norton III			10.87			
Spencer I	9.74	9.24-10.65	10.88	5.55	7.00	9.87
Spencer II	10.50	10.29-10.62	10.86	5.62	6.80	9.99
Spencer III	9.86	9.55-10.27	10.82	-	-	9.96
Spencer IV			10.93	5.77	6.92	-
Spencer V			10.83	-	6.98	10.04
Spencer VI-A			10.84	-	-	-
Spencer VI-B			10.80	-	-	-
Spencer VI-C			11.02	-	-	-
NUMEC I			10.91			
Sintered Comparison Specimens						
Davison I			10.79	-	-	-
MN I			10.68	-	-	-
Other Types of UO_2 for Comparison(d)						
WAPD sintered	10.27	10.19-10.34	10.40	5.25	6.55	9.70
HAPO sintered	10.74(e)	10.73-10.74	10.77	-	-	9.77
MCW PWR-Grade	-		9.88	2.99	4.56	8.11
MCW Micronized	-		-	2.27	3.11	-

(a) Denotes supplier and order number

(b) Measured by displacement of H_2O or CCl_4.

(c) Swaged density is influenced by mechanical and material variables, as described in DP-430(1) and DP-493.(2)

(d) The comparison materials are described in Appendix B.

(e) Volume computed from linear dimensions rather than displacement of mercury.

EFFECT OF PARTICLE SIZE ON DENSITY MEASUREMENTS

The pycnometer densities of a range of particle size fractions were measured (Table IIIa), but little effect of size was seen except for the extreme fractions. The smallest fractions (-200 mesh) tended to give lower densities because of procedural difficulties in measurement, while the density of the -1/4+6 mesh fraction of air-fused UO_2 was lower because the pieces were large enough to contain appreciable amounts of closed porosity.

Adding more fine particles to the typical particle size distribution of the pulverized samples increased the density of tapped specimens but had little effect on the density of poured and swaged specimens. Results are shown in Table IIIb. The effect of particle size on swaged density has been discussed in DP-430,(1) and the effect of particle size distribution on the densities of bulk specimens obtained by vibrational compaction was reported in DP-681.(3)

TABLE III

Effect of Particle Size on Density

a. Pycnometer Density by CCl_4 Displacement, g/cm^3

Particle Size Fraction(a)	Spencer I	Norton I and II	WAPD Sintered Pellets(b)
-1/4+6	-	10.65	10.47
-6+12	-	10.93	10.46
-12+20	-	11.03	10.49
-20+40	10.91	10.88	10.43
-40+70	10.86	10.72	10.31
-70+120	10.92	10.72	10.37
-120+200	10.86	10.85	10.54
-200+325	10.88	10.67	10.13
-325	10.82		

b. Density of Bulk Specimens, g/cm^3

Norton II, grade 2	Poured	Tapped	Swaged
-20 mesh (typical particle size distribution)(c)	5.78	6.83	9.92
-20 mesh + 5% of -200 mesh	-	7.17	9.82
-20 mesh + 10% of -200 mesh	5.84	7.42	9.82
-20 mesh + 15% of -200 mesh	5.83	7.57	-

(a) The particle size limits for each fraction are specified in terms of U. S. Standard Sieve sizes: -20+40, for example, includes those particles which went through a 20 mesh sieve (0.033 inch openings) but were held by a 40 mesh sieve (0.0165 inch openings). The sieve sizes were selected such that each fraction covered a size range of approximately a factor of two.

(b) See Appendix B for description.

(c) A typical particle size distribution of fused UO_2 pulverized to pass a 20 mesh sieve is as follows:

Size Limits	-20+40	-40+70	-70+120	-120+200	-200
Fraction, wt %	47	26	11	7	9

OXYGEN-TO-URANIUM RATIO

The fused UO_2 was seldom precisely stoichiometric, that is, it seldom had an oxygen-to-uranium ratio (O/U) exactly equal to 2.000. Inclusions of metallic uranium, uranium carbide, and uranium nitride were associated with a measured O/U <2.00. An O/U >2.00 indicated the presence of excess oxygen in the UO_2. It was possible to reduce excess oxygen content by a high temperature hydrogen treatment; process conditions for this reduction are discussed in Appendix C.

The O/U of fused UO_2 was not appreciably affected by exposure to ambient air; the experimental conditions and results are given in Appendix D.

The O/U was measured by the weight gain of the oxide on ignition to U_3O_8. The fractional weight gain yielded the quantity of oxygen required to reach U_3O_8 (O/U = 2.667) and thus permitted computation of the initial O/U of the sample. Stoichiometric UO_2 displays a 3.95% increase in weight on ignition.

Samples were crushed to pass a 70 mesh sieve before analysis. Larger pieces of UO_2 tended to cause error by spattering fragments of UO_2 out of the boat as the pieces fractured during oxidation to U_3O_8.

VARIABILITY

The O/U's were found to vary among the suppliers and from order to order from a given supplier; in some cases there were large variations within a single order. The averages and ranges of O/U's of the materials received are listed in Table IV.

Uranium oxide fused under inert gas (Spencer) was fairly uniform in O/U within a given order; there were significant differences between orders, however.

The air-fused oxide (Norton) was more variable than that fused under protective atmosphere, but control of the O/U improved with each successive order. The average O/U decreased from 2.14 for the Norton I order to 2.08 for the Norton II order to 2.001 for the Norton III order.

The Norton III order was much less variable in O/U from lot to lot than the first and second orders. The Norton III order consisted of 54 lots of about 100 pounds each: five preliminary exploratory lots and 49 lots in the main part of the order. Four of the five exploratory lots were analyzed

TABLE IV

Oxygen-to-Uranium Ratios

Designation[a]	O/U Average	O/U Range
Norton I	2.14	2.00 -2.19
II	2.08	1.99 -2.25
III	2.001	1.949-2.029
Spencer I	2.013	2.004-2.029
II	1.971	1.960-1.985
III	2.004	2.002-2.007
IV	2.008	1.988-2.017
V	1.999	1.989-2.005
VI-A	2.000	1.997-2.005
VI-B	2.001	1.997-2.008
VI-C	1.944	1.937-1.951
NUMEC I	2.012	2.008-2.015
Sintered Comparison Specimens		
Davison I	2.025	-
MN I	2.005	-

---

[a] Denotes supplier and order number.

as substoichiometric because of nitride, carbide, and metallic uranium inclusions. Forty-four of the remaining 49 lots had O/U's lying within the range of 2.00 to 2.03. Figure 3 shows the frequency distribution of lots according to O/U for the complete Norton III order.

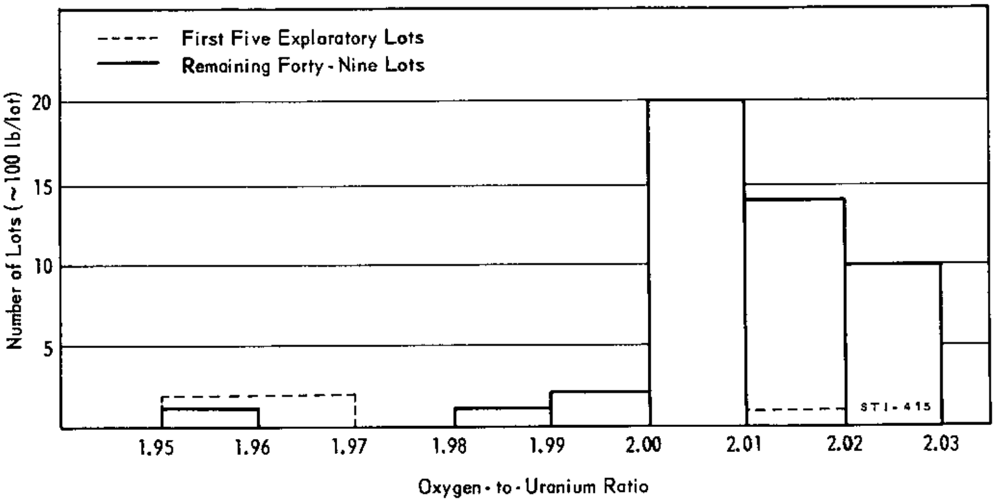


FIG. 3 OXYGEN-TO-URANIUM RATIOS IN THE NORTON III ORDER

ASSOCIATION WITH APPEARANCE

The appearance of the air-fused UO_2 was associated with excess oxygen content to some extent. Large shiny crystals (grade 1 in Figure 2) tended to have O/U's that were approximately 2.00, while irregular, cratered pieces (grade 5 in Figure 2) contained substantial amounts of excess oxygen.

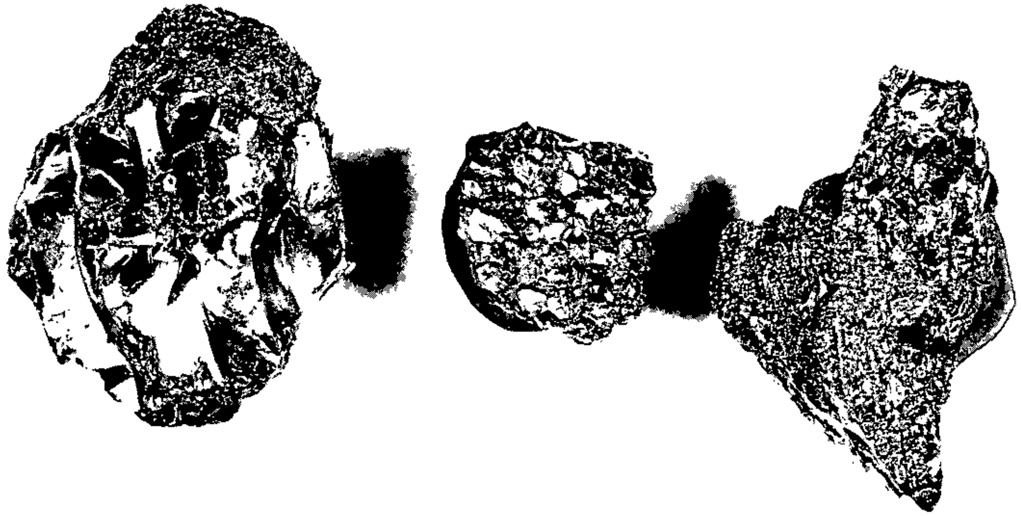
The entire contents of three drums (4, 17, and 28) from the Norton II order, and selected specimens from each drum in the Norton I order and the remaining drums of the Norton II order were graded and analyzed. Comparisons of grades with O/U are shown in Table V.

TABLE V

Oxygen-to-Uranium Ratios of Graded Air-Fused UO_2

			Norton II Order			
	Norton I Order		All Drums		Drums 4, 17, and 28 Only	
Grade	Avg	Range	Avg	Range	Avg	Range
1	2.058	2.007-2.088	2.056	1.992-2.080	2.024	1.992-2.080
2+	2.142	2.130-2.188	2.096	2.026-2.170	2.060	2.042-2.071
2	2.145	2.101-2.186	2.063	2.004-2.131	2.043	2.018-2.094
2-	2.192	-	2.039	1.986-2.093	2.022	2.006-2.043
3	2.193	-	-	-	-	-
4	2.206	-	-	-	-	-
5	-	-	2.113	2.013-2.250	2.104	2.014-2.136

Detailed examination of the drum 4 oxide from the Norton II order showed that it was of exceptionally high quality. The average O/U was good, and the range of O/U's was narrow. Nearly all the oxide was grade 1, but there were minor variations that warranted subclassification. Examples of the subclassifications are shown in Figure 4. Examination and analysis of drum 4 yielded the results in Table VI.



Grade 1 Grade 1D Grade 1E

Neg. 45477

Grade 1 – Large, smooth crystals
Grade 1D – Small, equiaxed crystals
Grade 1E – Small crystals aligned in a striated pattern

FIG. 4 SUBCLASSIFICATIONS OF GRADE 1 AIR-FUSED UO_2, 1X
Drum 4, Norton II Order

TABLE VI

Oxygen-to-Uranium Ratios of UO_2 from Drum 4, Norton II

	O/U	
Grade	Average	Range
1D	2.009	1.992-2.022
1E	2.039	2.022-2.048
1	2.005	1.998-2.014
All grades	2.014	1.992-2.048

The variations in O/U in the subclassifications were much smaller than those in the different grades for the order taken as a whole. With the exception of the drum 4 subclassifications, the range in each grade was found to be too great to allow reliable visual selection of a desired O/U.

EFFECT OF O/U ON PARTICLE FRIABILITY

An apparent hardening or toughening of the oxide, making it more resistant to crushing, was observed generally in specimens with O/U >2.00. This increased resistance to crushing, revealed in two different experiments, seemed to stem from appreciable amounts of second-phase impurity.

Friability Test

A test for friability measured the load required to compress a fixed weight of sample to a specified final volume. The experimental arrangement is shown in Figure 5. The method gave the average friability of a large number of particles in a single test. A narrow particle-size range, -18+20 mesh, gave the most reproducible results.

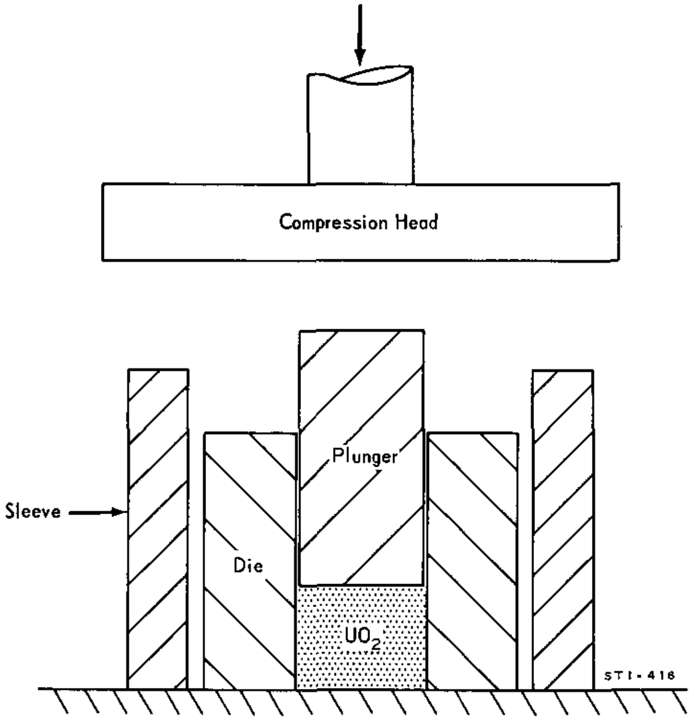


FIG. 5 FRIABILITY TEST ASSEMBLY

The most friable samples (requiring the least load for the specified compaction) were nearly stoichiometric UO_2; the less friable samples each contained appreciable second-phase impurity, U_4O_9 for samples 4 to 6 and uranium metal for sample 1 (see Table VII). This observation suggests a hardening or toughening effect of the second phase analogous to that sometimes observed in metals.

TABLE VII

Friability of Fused UO_2 Samples

	Sample	O/U	Final Load, lb	
			Average	Range
1.	Spencer II	1.973(a)	1100	1075-1125
2.	Norton II	2.014	975	900-1050
3.	Norton II	2.020	980	900-1050
4.	Norton II	2.038	1175	1150-1210
5.	Norton II	2.060	1025	975-1050
6.	Norton II	2.064	1095	990-1100

(a) Contained metallic uranium inclusions.

Classification by Crushing

A classification into two O/U groups was made by pulverizing and sieving samples of the oxide. Oxide of O/U ≈2.03 was pulverized to -20 mesh by a Braun pulverizer, and then sieved into +120 mesh and -120 mesh fractions. Analysis yielded O/U = 2.03 for the +120 mesh fraction, which accounted for about 75% of the material, and O/U = 2.00 for the -120 mesh fraction. When the +120 mesh fraction was pulverized to -120 mesh, it still analyzed O/U = 2.03; thus the effect of particle size, as such, in the analysis was eliminated.

From its predominance in the -120 mesh fraction after the initial crushing, single-phase, stoichiometric UO_2 apparently pulverizes more readily than UO_2 with regions containing a U_4O_9 phase. This observation provides an independent confirmation of the greater friability of stoichiometric fused UO_2. It also suggests a possible mechanical means of isolating stoichiometric UO_2.

INCLUSIONS

Certain impurities were present in sufficiently large amounts to form inclusions clearly visible under the optical microscope. Those identified were U_4O_9, metallic uranium, UC, and UN_2.

Microappearance, microhardness, and susceptibility to attack by air or acid were useful in the classification of the microscopic inclusions. Positive identification was made by X-ray diffraction analysis. Table VIII lists characteristics of the various inclusions that are useful in their identification. The results for UC can be compared with those reported by Kehl(4) for inclusions in uranium; the microhardness and speed of discoloration by nitric acid agree, but the rapid air tarnishing reported by Kehl was not observed.

TABLE VIII

Characteristics of Inclusions in Fused UO_2

	U	UC	UN_2	U_4O_9	UO_2
"Tukon" Microhardness, DPH[a]					
Average	220	650	820	750	580
Range	200-240	610-710	710-930	670-840	500-610
Microappearance					
As-polished	White	White	White	Indistinguishable from UO_2	Gray
Tarnished one day	Gold or brown	White	White	Indistinguishable from UO_2	-
Etched 20 sec with H_2O_2 + H_2SO_4	Slight darkening. Uniform gold	Darkening. Multicolored (blue, green, orange, red, brown)	White	Dark gray, distinguishable from UO_2	-
Etched in 1:1 HNO_3					
10 sec	No effect	Vigorous reaction and obvious darkening of second phase (some undarkened lines in second phase)	No effect	No effect	-
30 sec	No effect	All black or brown except for a few white lines	No effect	No effect	-
60 sec	Scattered gold tinge	Brown spots turning red or blue	No effect	Faintly discernible	-
3 min	Little change	Black	Pitting begins	Distinguishable from UO_2	-

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(a) Diamond Pyramid Hardness numbers measured on a "Tukon" microhardness tester using a 50 g load.

Survey microexaminations of polished cross sections of pieces randomly selected from each order gave a qualitative measure of the various inclusions present. The results of these microexaminations are tabulated in Table IX, where the frequency of appearance of each type of inclusion is listed.

TABLE IX

Frequency of Inclusions in Fused UO_2

		Frequency of Inclusions[b] in Pieces Examined, %				
		U_4O_9				
Designation[a]	No. of Pieces Examined	Generally Distributed	Trace	U	UN_2	UC
Norton I	10	100		ND[c]	ND	10
Norton II						
Drum 4	54	43	22	6	9	37
Drums 17 and 28	24	83	12	4	ND	17
Norton III						
Exploratory (320 lb)	70	29	37	29	49	9
Remainder (4780 lb)	158	44	32	2	25	42
Spencer I	22	14	59	18	18	ND
Spencer II	40	12	8	68	15	2
Spencer III	94	44	38	11	11	13
Spencer IV	69	41	46	22	13	4
Spencer V	20	35	40	25	5	25
Spencer VI-A	12	8	75	25	8	ND
VI-B	12	-	92	8	ND	ND
VI-C	12	-	17	100	8	ND
NUMEC	88	ND	ND	ND	5	ND
Sintered Comparison Specimens[d]						
	30	ND	ND	ND	67[e]	ND

(a) Denotes supplier and order number. There were 5 exploratory lots and 49 argon-cooled lots in the Norton III order.

(b) In most cases, inclusions were too small to permit positive identification by X-ray diffraction analysis. Identification was usually based on metallographic techniques, such as tarnishing and etching behavior.

(c) ND = none detected

(d) The Davison oxide particle size was too small to be mounted and polished by the usual methods for examination of inclusions; no data could be obtained.

(e) There is some doubt as to the identity of these inclusions. Although the tarnishing and etching behavior were appropriate for UN_2, the microhardness was too small; unfortunately, only a few of these inclusions were large enough for microhardness measurements.

EXCESS OXYGEN

An excess oxygen phase (U_4O_9) was nearly always present to some extent, even when it did not affect the O/U analysis much. It was sufficiently general in the Norton I order and in drums 17 and 28 of the Norton II order to increase the O/U significantly (see Table IV).

The U_4O_9 phase was revealed by microexamination of samples polished and etched with an H_2O_2-H_2SO_4 etchant,* and it was identified by X-ray diffraction methods. In some cases this phase was uniformly distributed throughout the matrix, while in other cases it was concentrated at edges and in cracks. When it was uniformly distributed, the amount of U_4O_9 phase measured by lineal analysis agreed fairly well with the amount found by O/U analysis. Photomicrographs corresponding to various O/U's are shown in Figure 6.

EXCESS URANIUM

Metallic uranium inclusions were prominent in the Spencer II and Spencer VI-C orders. The Spencer VI-C order was a sample lot supplied to show that large amounts of metallic uranium inclusions could be produced by suitable process control. Preliminary indications of excess uranium content were given by the O/U's, which were 1.97 for Spencer II and 1.94 for Spencer VI-C.

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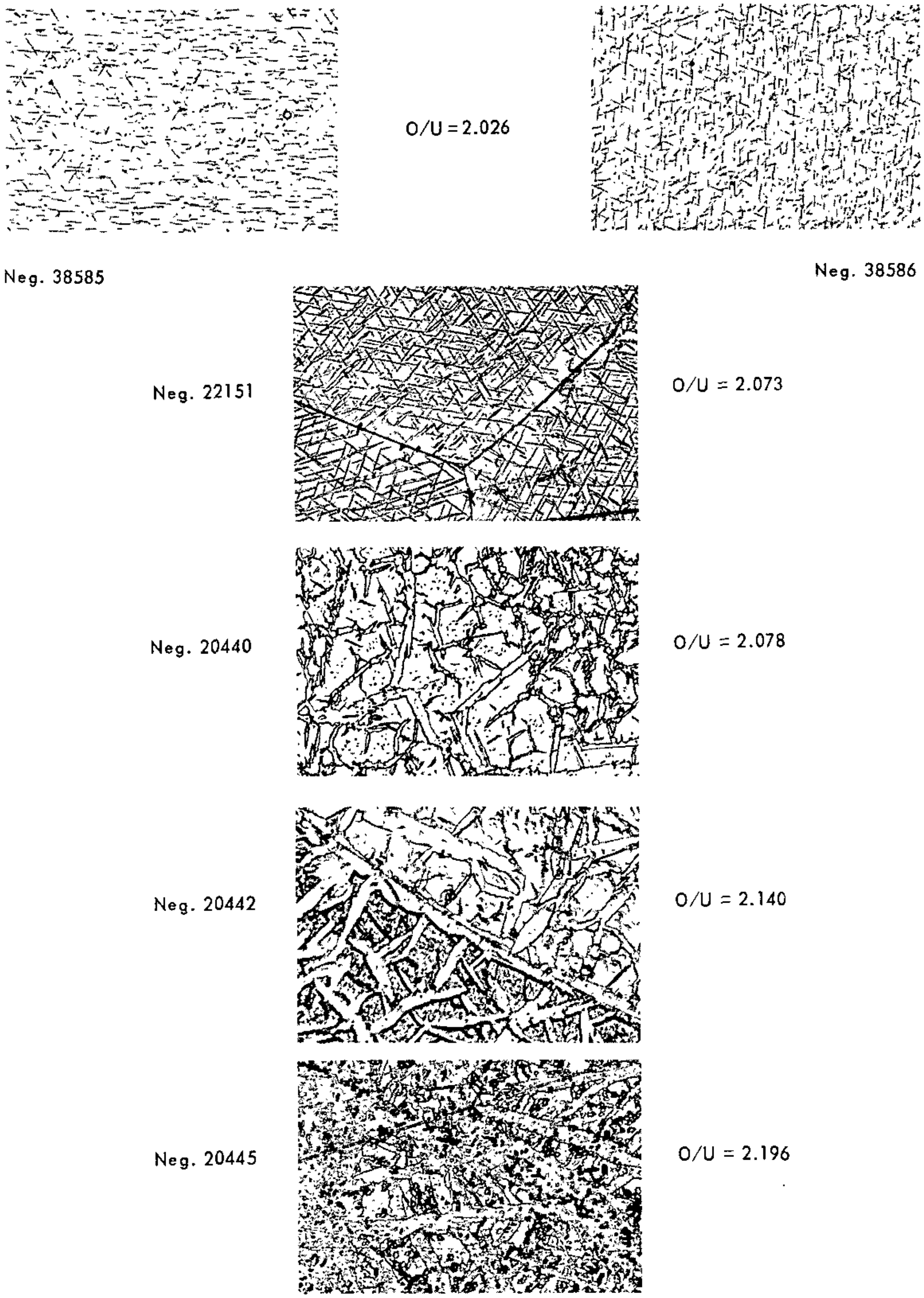
* Etchant was a mixture of one part concentrated H_2SO_4 with nine parts of a 30% solution of H_2O_2.



Neg. 38585

O/U = 2.026

Neg. 38586

Neg. 22151

O/U = 2.073

Neg. 20440

O/U = 2.078

Neg. 20442

O/U = 2.140

Neg. 20445

O/U = 2.196

FIG. 6 FUSED UO_2 WITH EXCESS OXYGEN, 200X

Polished and Etched

Microexamination of the as-polished samples showed a white phase that turned gold or brown after a day's exposure to ambient air. The metallic uranium inclusions appeared in a variety of shapes. Figures 7 and 8 show uranium in irregular patterns, in regular geometric shapes, and in dendritic patterns. Voids were usually associated with the uranium inclusions.

Available data(5) suggest that substoichiometric UO_2 is stable at the fusion temperature if there is no overpressure of oxygen. The substoichiometric UO_2 dissociates on cooling into UO_2 and metallic uranium.

A dendritic pattern, as in Figure 8, is commonly understood to form before the matrix solidifies, but uranium metal could not have solidified before the UO_2 during cooling because of its lower melting point. A mechanism which might have produced this dendritic growth is given in Appendix E.

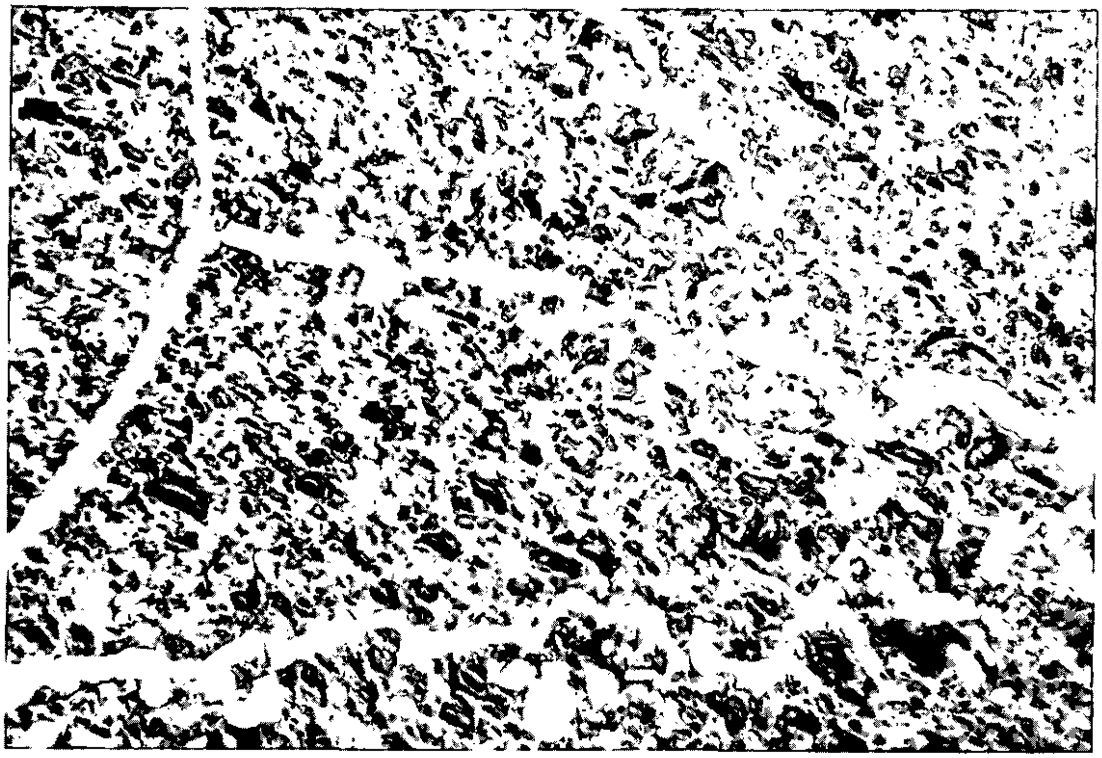
URANIUM CARBIDE

The uranium monocarbide was visible in the as-polished condition as a white phase of smooth and rounded appearance (Figure 9a). The UC phase turned dark after a few seconds in nitric acid (Figure 9b), but then fine lines appeared in it that were not seen in the as-polished condition. On the basis of comparison with micrographs published by Secrest(6) these lines appeared to be UC_2, but the quantity was too small for identification by X-ray diffraction.

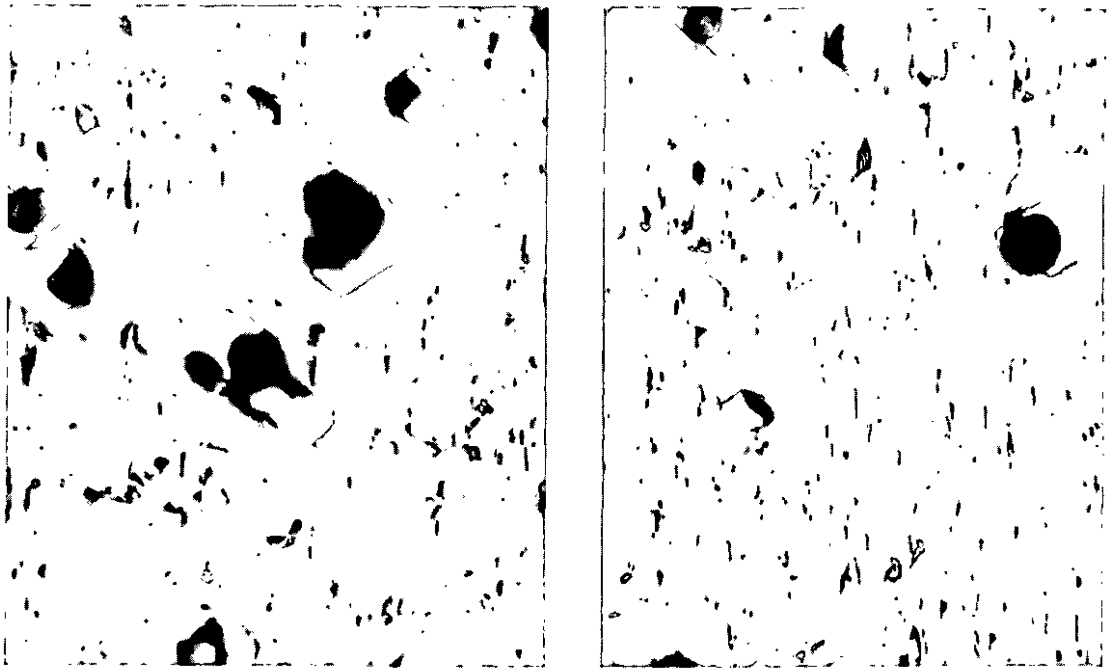
A few pieces of UO_2 contained large amounts of UC; traces of it were widespread. The source of carbon was probably the graphite electrodes employed in the fusion process. Attention was first drawn to the pieces containing substantial amounts of UC because they sparked or gave off a transitory orange glow when struck.

URANIUM NITRIDE

Uranium dinitride appeared as a white, often acicular phase (Figure 10). *According to data reported by Kehl the* microhardness and speed of attack by nitric acid on typical inclusions in uranium metal suggested that the inclusions were U(N,C) high in N, but X-ray analysis indicated a cubic lattice parameter of 5.318 Å, corresponding to UN_2 or to substoichiometric UN_{2-x}. Kehl gives no data for UN_2.

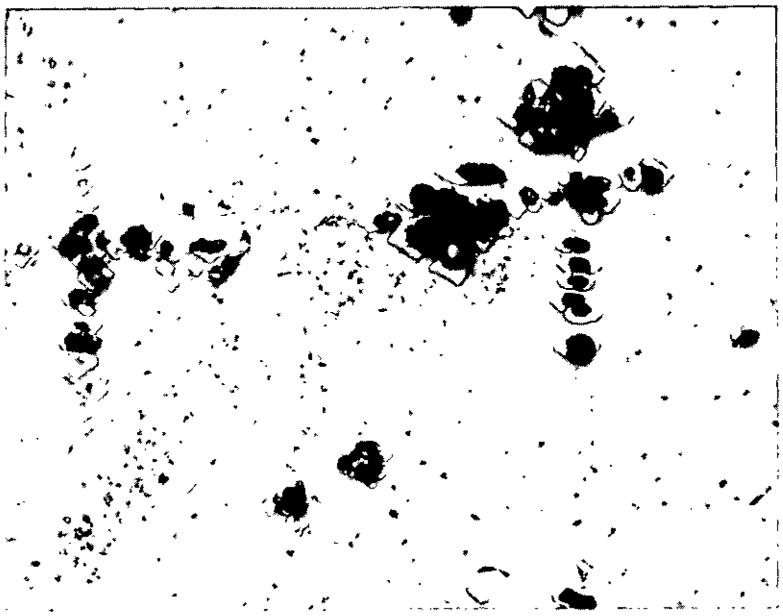


Neg. 28345 250X



Neg. 34377 500X Neg. 34376 500X

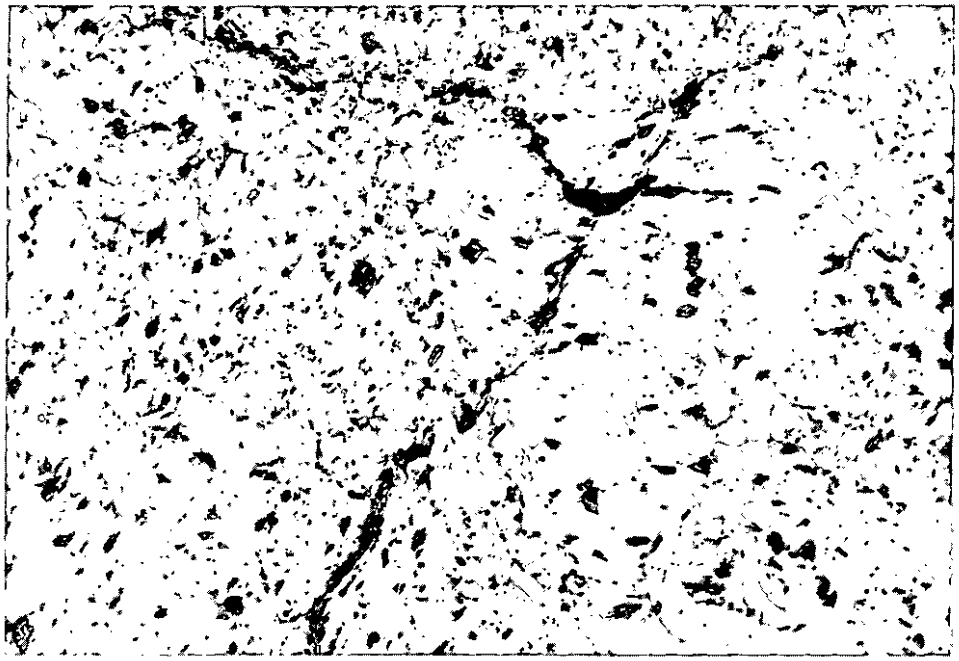
FIG. 7 URANIUM METAL INCLUSIONS IN FUSED UO_2
As-polished



Neg. 34088

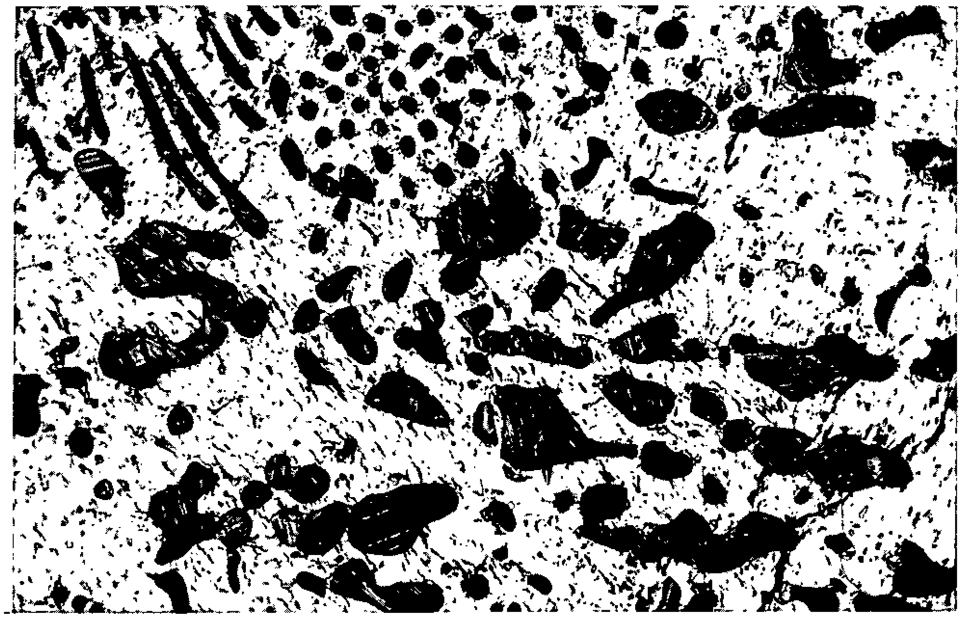
Neg. 34090

FIG. 8 DENDRITIC URANIUM INCLUSIONS IN FUSED UO_2, 250X
As-polished



Neg. 34078

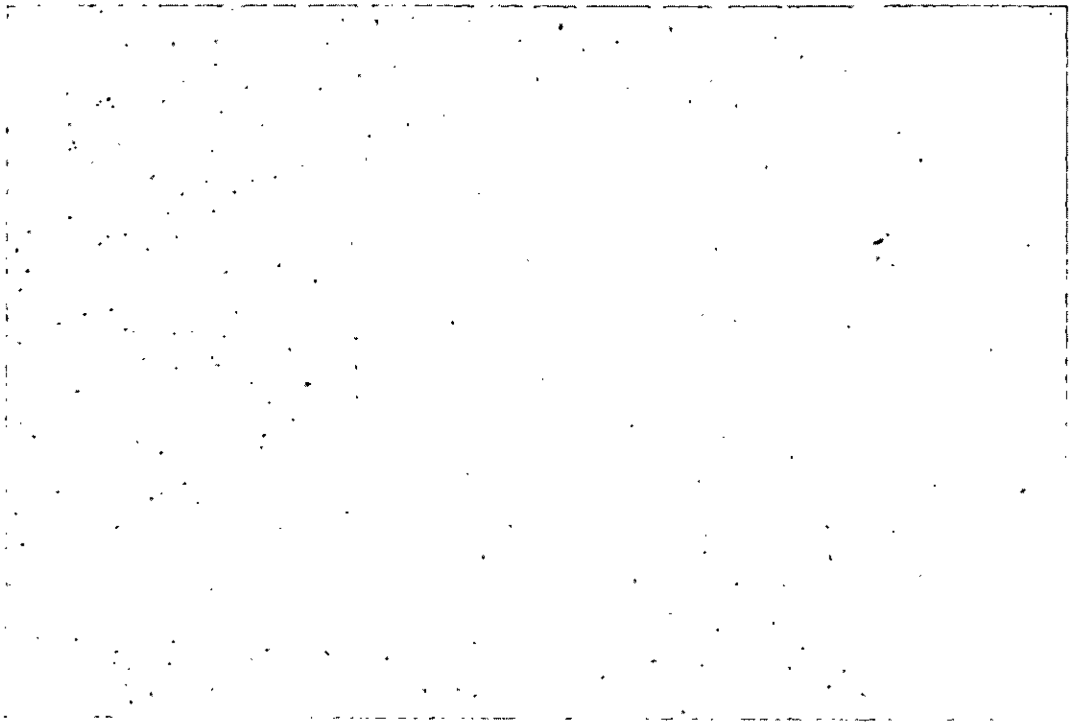
a. As-polished



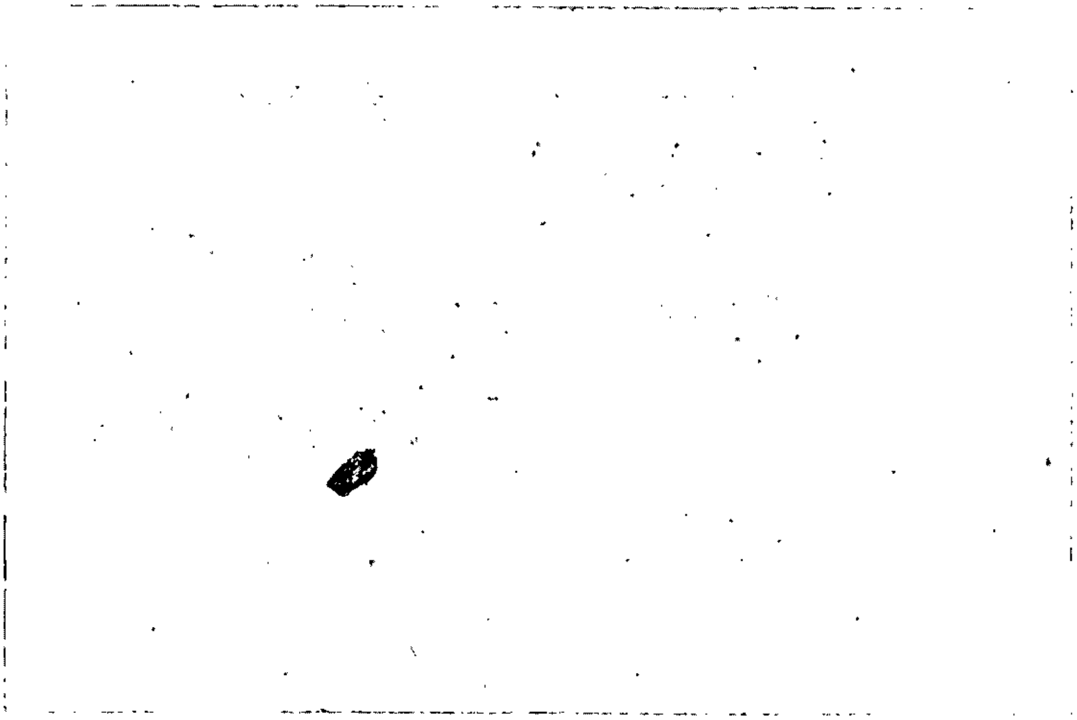
Neg. 34373

b. HNO_3 Etch

FIG. 9 UC INCLUSIONS IN FUSED UO_2, 250X



Neg. 30238



Neg. 30236

FIG. 10 UN_2 INCLUSIONS IN FUSED UO_2, 250X
As-polished

TRACE METALLIC IMPURITIES

Trace metallic impurities were determined by emission spectrography (see Table X). Aluminum, iron, and silicon were the major impurities not specifically associated with microscopic inclusions. Concentrations ranged up to 160 ppm aluminum, 440 ppm iron, and 200 ppm silicon. Smaller amounts of chromium, copper, nickel, lead, and manganese were detected. Tin, magnesium, and vanadium were present in quantities ranging from 10 to 20 ppm in some cases. Contamination by elements of high neutron cross section was low, typically $\leqslant$0.6 ppm for each of boron, cadmium, and silver.

TABLE X

Trace Metallic Impurities

(Measured by emission spectrography on as-received oxide)

Designation(a)		Average Impurity Content, ppm							
		Al	Fe	Si	Cr	Cu	Ni	Pb	Mn
Norton	I		440						
	II		310	50				40	
	III	160	360	90	10	15	8	5	25
Spencer	I		90	50		5			
	II(b)	100	340	150	5	20	20	65	80
	III(b)	100	220	100	7	45	15	110	
	IV	135	60	160	5	7	15	9	10
	V	15	40	40	5	55	8	5	
	VI-A VI-B VI-C (c)	15	20	10	5	5	10	5	
NUMEC		50	20	160	5	60	10	10	10
Sintered Comparison Specimens									
Davison		75	80	200	15	5	5	10	10
MN		100	300	150	70	8	25	20	30

(a) Denotes supplier and order number.

(b) These analyses were made on oxide that had been through the fuel element fabrication process, where some impurities may have been added. This appears probable particularly for iron, because the postfabrication iron content was considerably higher than that in the same supplier's orders analyzed in the condition received.

(c) Lots A, B, and C were essentially identical in content of trace metallics, so they are lumped together here.

SORBED GASES

Gases were desorbed from fused UO_2 when it was heated in a vacuum. The principal gases released at 1000 and 1300°C were hydrogen, nitrogen, carbon monoxide, and carbon dioxide.

Studies of gaseous impurities were begun after unexpected amounts of N_2 and CO_2 were found within swaged rods of fused UO_2 following preliminary irradiation tests.(7-9) Release of sorbed gases by UO_2 at the high fuel temperatures experienced during reactor operation could cause fuel element rupture by the buildup of internal pressure or by side reactions of the released gas; as an example of the latter effect, hydrogen freed within the fuel element can be absorbed by the zirconium sheath material and cause brittle fracture.(10)

The amount of gas released by the UO_2 during vacuum extraction depended on the temperature of extraction and on the type and particle size of UO_2. The amount of gas extracted increased as the temperature was increased and the particle size was decreased, suggesting a diffusion-controlled mechanism of gas release. Results of vacuum extraction at 1000 and 1300°C are shown in Table XI. Differences among UO_2 from different sources and among different orders of UO_2 from the same source can be seen. The increase of gas release with decrease in particle size was attributed to the shorter distance that internally held gases had to diffuse before they could escape from the particles during extraction.

Another explanation of the effect of particle size on gas release is that the gas was simply adsorbed on the UO_2 particle surfaces, but two things argue against it. (1) The fine-particle samples were crushed in an argon-filled gloved box to minimize the chances of contamination by atmospheric gases, and no appreciable quantity of argon was released from the samples on subsequent vacuum extraction. (2) Only a small quantity of gas would be expected from simple surface adsorption. If the entire surface of the particles were covered with a monomolecular layer of gas, the amount would be much less than that observed on extraction. For example, taking the average particle diameter of -120+200 mesh particles as 100 microns and allowing 20 square Angstrom units of surface area per molecule, one computes 0.001 cc of adsorbed gas per gram of UO_2. Allowance for the actual irregular shapes of the particles (rather than ideal spheres) might double this result, but even that is only 1/25 as much as 0.05 cc/g, the smallest gas release listed in Table XI for -120+200 mesh particles.

TABLE XI

Gases Desorbed from UO_2

		Vacuum Extraction at 1000°C					Vacuum Extraction at 1300°C				
		Total Gas,	Major Constituents of the Gas, ppm				Total Gas,	Major Constituents of the Gas, ppm			
UO_2 Specimen	Particle Size[(a)]	cc/g	H_2	N_2	CO	CO_2	cc/g	H_2	N_2	CO	CO_2
Norton II, Drum 4, Grade 1D	-40+70[(a)]						0.25	3	220	40	3
	-120+200						0.40	7	260	100	12
	-325						0.72	18	380	160	40
Norton II, Drum 17, Grade 5	-20	0.07	2	16	40	5					
	-40+70						0.07	5	4	20	1
	-120+200						0.13	4	9	80	7
	-325						0.49	20	30	270	40
Spencer II	-20	0.04	2	5	10	2					
	-40+70	0.18	10	5	50	6					
	-120+200	0.17	10	5	30	4					
	-325	0.66	40	80	100	15	0.30	10	130	40	3
Spencer III	-20	0.09	3	39	20	20					
	-40+70	0.04	2	11	11	3	0.12	7	20	10	2
	-120+200	0.08	4	8	20	20					
	-325	0.27	6	80	20	230	0.60	15	120	310	150
Spencer IV	-40+70	0.02	1	6	3	2	0.06	-	70	-	-
	-120+200	0.05	1	20	12	8	0.32	4	110	150	20
	-325	0.19	5	100	40	35	0.24	4	150	70	10
Spencer V	-20	0.11	5	35	35	12					
	-400+70						0.13	-	170	43	-
	-120+200						0.29	-	290	95	-
	-325						0.40	2	320	130	10
Spencer VIA	-40+70	0.04	1	15	10	4					
	-325	0.27	10	30	80	110	0.30	1	230	30	100
Spencer VIB	-40+70	0.07	3	13	20	12					
	-120+200	0.08	1	50	9	6					
	-325	0.18	5	50	40	65	1.04	50	250	250	40
Spencer VIC	-40+70	<0.02	ND	11	2	8					
	-120+200	0.09	5	15	10	14					
	-325	0.28	20	10	30	30	0.22	16	15	15	7
NUMEC	-40+70	0.01	0.7	ND	2	0.1					
	-120+200	0.06	3	7	20	6					
	-325	0.19	7	9	70	60	0.06	-	12	40	30
Sintered Comparison Specimens											
Davison	-40+70	0.09	5	1	20	2					
	-120+200	0.08	1	30	20	20					
	-325	0.13	3	3	30	110	0.36	11	5	160	130
MN	-40+70	0.04	2	2	20	2					
	-120+200	0.06	3	2	20	7					
	-325	0.18	8	5	40	70	0.20	8	13	80	50

(a) Particle sizes according to U. S. Standard Sieve sizes.

A study of the effect of time was not made because of equipment limitations. Typically, the gas came off rapidly during the first stages of extraction, and the rate diminished with time. After about 15 minutes, the rate of gas release was not measurable with the equipment used. Evidently the gases near the particle surfaces were released quickly, but subsequent release was slower because the gases had to diffuse from within the particles to the surface.

There is no good reason to believe that all the gases were extracted from any sample, since neither temperature increase nor particle-size reduction was carried far enough to produce a distinct plateau of gas evolution.

Studies of the gas content of fused UO_2 are continuing with higher temperatures of vacuum extraction and other methods of analysis.

G R Cole
G. R. Cole

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APPENDIX A

UO_2 SUPPLIERS

Fused UO_2

Norton	The Norton Company, Worcester, Massachusetts; process done at the company's plant in Chippawa, Ontario.
Spencer	The Spencer Chemical Company, Kansas City, Missouri; process done at the company's plant in Military, Kansas.*
NUMEC	Nuclear Materials and Equipment Corporation, Apollo, Pennsylvania.

Sintered UO_2 Used for Comparison

Davison	The Davison Chemical Company, Erwin, Tennessee; a division of W. R. Grace and Company.
MN	Mallinckrodt Nuclear, Hematite, Missouri; a division of Mallinckrodt Chemical Works.**

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* The UO_2 fusion facility of the Spencer Chemical Company has been sold to Kerr-McGee Oil Industries, Inc., of Oklahoma City, Oklahoma.

** Mallinckrodt Nuclear is now a part of United Nuclear Corporation.

APPENDIX B

SUPPLIERS AND DESCRIPTIONS OF NONFUSED UO_2 USED FOR DENSITY COMPARISON

Density data from nonfused UO_2 were included in Table II for comparison with fused UO_2. The comparison materials were:

WAPD Sintered	Sintered pellets manufactured for the first core loading of the PWR, but rejected because of chips or other minor defects. From the Bettis Plant, a division of Westinghouse Electric Corporation, Pittsburgh, Pa.
HAPO Sintered	Large sintered discs made to be crushed to provide feed material for swaging studies. From J. J. Hauth, of the Hanford Laboratories Operation, Hanford Atomic Products Operation, Richland, Washington.
MCW PWR-Grade	UO_2 used to make the sintered pellets for the blanket of the first PWR core. The applicable specification is WAPD-FE-848, Rev. 2(11). From Uranium Division, Mallinckrodt Chemical Works, Weldon Spring, Missouri.
MCW Micronized	PWR-grade powder subjected to a fluid jet grinding process to reduce the particle size.

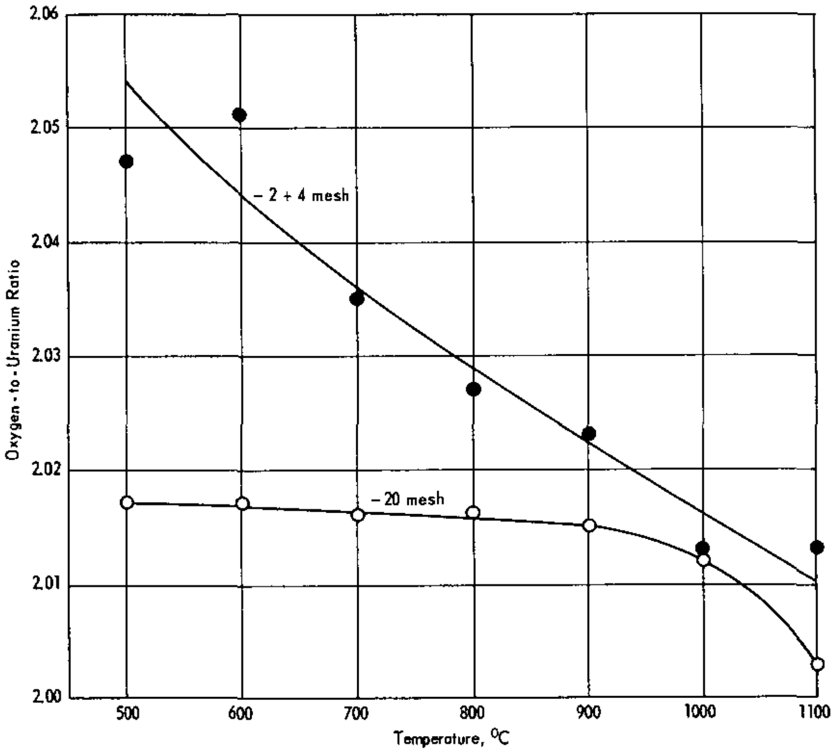
APPENDIX C

REDUCTION OF NONSTOICHIOMETRIC UO_2

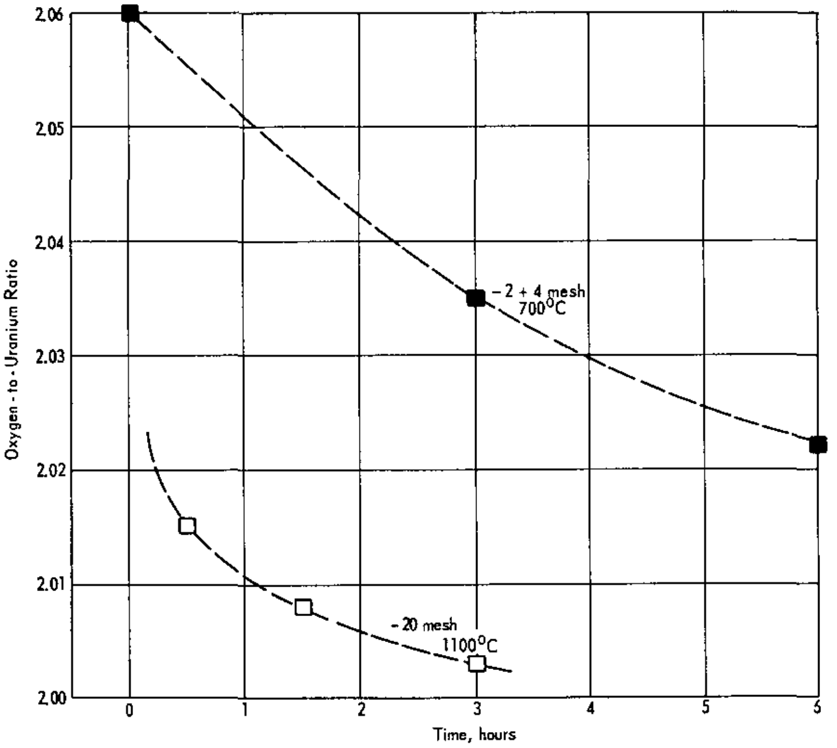
There is a possibility that reduction of the nonstoichiometric oxide sometimes produced by the low cost, air-fusion process can be performed cheaply enough to make the total process economically competitive. A survey of some of the variables involved in a hydrogen reduction process was generally encouraging.

Smaller particles were reduced in O/U by shorter soaking times or at lower temperatures than were larger particles, as would be expected if the rate of reduction was diffusion controlled. Effects of time and temperature on two different ranges of particle size are shown in Figure C-1. Minus 20 mesh $UO_{2.06}$ was reduced to $UO_{2.017}$ by heating in hydrogen for three hours at 500°C. The same treatment reduced larger particles, -2+4 mesh, to only $UO_{2.05}$. A temperature of 1100°C was required to reduce -2+4 mesh $UO_{2.06}$ to $UO_{2.013}$ in three hours. At this temperature -20 mesh particles were reduced to $UO_{2.015}$ in 1/2 hour, $UO_{2.008}$ in 1-1/2 hours, and $UO_{2.003}$ in 3 hours. In all these cases the oxide was quenched to approximately 140°C in nitrogen following the hydrogen soak.

Several methods of cooling the UO_2 were tried. Quenching in nitrogen was the most satisfactory way of retaining the UO_2 in the reduced state after reduction in hydrogen. Slow cooling in nitrogen resulted in resorption of excess oxygen (either from a small leak in the furnace or from impurities in the tank nitrogen) to an O/U of 2.05 for -20 mesh oxide. A 1/2-inch piece that was given this treatment was heavily oxidized near the edge, but was free of U_4O_9 phase in the center. This demonstrated that the particle had been thoroughly reduced and was reoxidized subsequently. Quenching in air was unsatisfactory because of rapid resorption of the readily available oxygen of the air to an O/U of 2.11, higher than that of the original material. Slow cooling in hydrogen achieved the same result as quenching in nitrogen (O/U $\sim$2.015), but it was inconvenient from an operational standpoint.



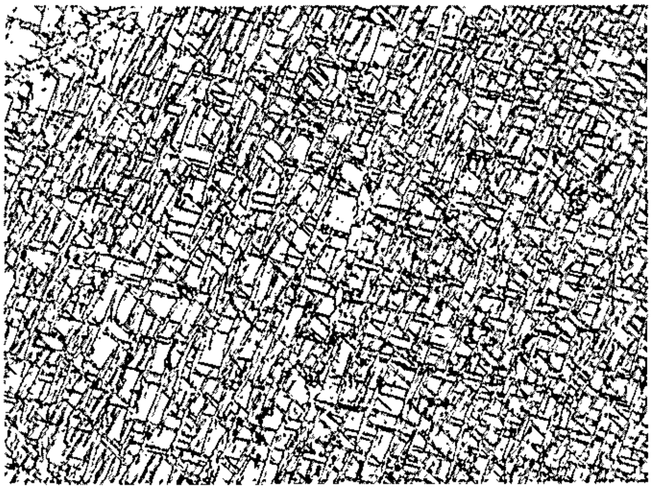
Effect of Temperature
Samples held in hydrogen for three hours and then quenched in nitrogen



Effect of Time

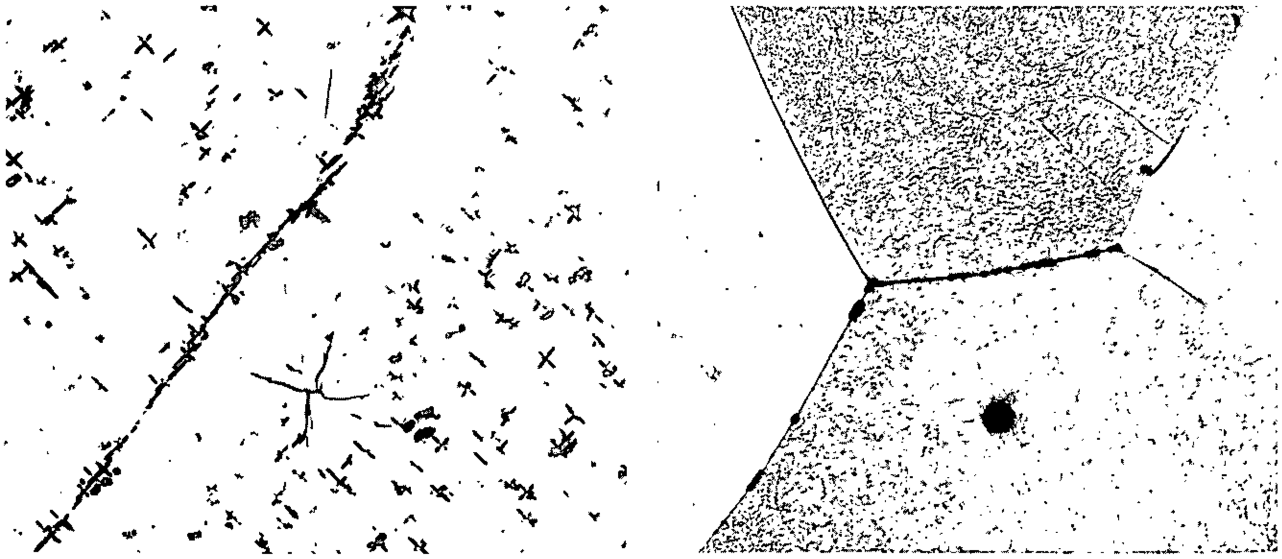
FIG. C - 1 HYDROGEN REDUCTION OF EXCESS OXYGEN IN FUSED UO_2
(Initial O/U = 2.06)

Figure C-2 compares the original microstructure with the postreduction microstructure, both slow cooled in hydrogen and quenched in nitrogen. The final O/U was the same in both cases, but the microstructures due to the excess oxygen were different. The slow-cooled specimen had a characteristic crosshatched U_4O_9 structure, while the quenched specimen obviously cooled too rapidly for orderly recrystallization of U_4O_9.



Neg. 29847

Starting Material. O/U = 2.06



Neg. 30211

Slow cooled in hydrogen after reduction. O/U = 2.014

Neg. 30965

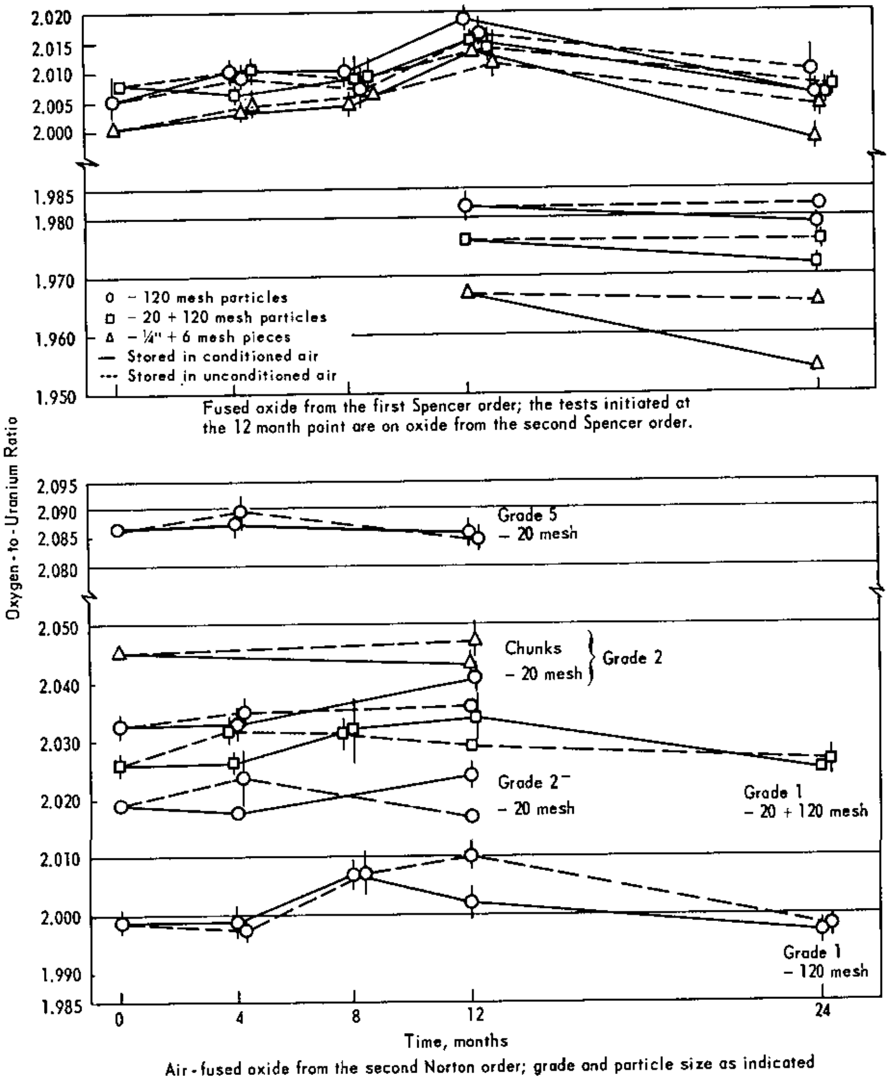
Quenched in nitrogen after reduction. O/U = 2.014

FIG. C-2 STRUCTURE OF U_4O_9 PHASE IN FUSED UO_2 BEFORE AND AFTER HYDROGEN REDUCTION, 250X
Polished and Etched

APPENDIX D

EFFECT OF AMBIENT AIR ON EXCESS OXYGEN CONTENT

Fused UO_2 exposed to ambient air did not oxidize appreciably over periods up to two years. Various grades, types, and particle sizes of fused UO_2 were exposed to both conditioned (nominally 70°F, 50% relative humidity) and unconditioned air; samples were withdrawn for analysis at regular intervals. The data are shown in Figure D-1. The analytical precision claimed for an individual analysis was ±0.005, but each point represents four or six duplicate determinations. The vertical line through each point indicates the range $\pm\sigma$.



Fused oxide from the first Spencer order; the tests initiated at the 12 month point are on oxide from the second Spencer order.

Air-fused oxide from the second Norton order; grade and particle size as indicated

FIG. D-1 EFFECT OF STORAGE ON FUSED UO_2

A decrease in the excess oxygen in UO_2 exposed to ambient air would certainly not be expected, so the generally occurring drop in O/U at 24 months following the slight increase in 12 months probably indicates a systematic error in analysis.

The larger pieces sometimes showed lack of uniformity in O/U; sample nonuniformity is probably responsible for the divergence between the Spencer-fused -1/4+6 mesh pieces at 24 months (see Figure D-1), for example. A much more extreme case of nonuniformity (not graphed) was shown by coarse pieces of air-fused Norton grade 2 oxide. The initial analysis was O/U = 2.045 (σ = 0.001), but the samples analyzed after four months had O/U = 2.015 (σ = 0.003) in conditioned air and 2.005 (σ = 0.002) in unconditioned air. Each sample was pulverized to -70 mesh and mixed well in preparation for analysis, which accounts for the good agreement in the duplicate determinations as expressed by the small values of σ.

APPENDIX E

PROPOSED MECHANISM FOR GROWTH OF DENDRITIC URANIUM INCLUSIONS IN UO_2

Limited knowledge of high temperature behavior of uranium-oxygen systems prevents any positive conclusions as to the mechanism producing dendritic growth of uranium in UO_2; however, a possible mechanism is:

1. The UO_2 was held above the melting point with low over-pressure of oxygen during arc fusion (vacuum or inert gas cover) and some oxygen was lost, resulting in fewer than two oxygens per uranium atom. (Such behavior has been reported by Anderson(5), et al.)

2. On cooling, the melt first passed through a phase region, solid suboxide + liquid UO_2, where a lower oxide than UO_2 (say UO) froze out in a dendritic pattern at a temperature greater than the fusion temperature of UO_2, and then passed through a phase region, solid suboxide + solid UO_2, where the UO_2 matrix solidified as the temperature decreased further.

3. At some lower temperature the suboxide disproportionated to UO_2 and metallic uranium. The disproportionation was accompanied by considerable shrinkage, which accounted for the void space usually seen with the uranium inclusions. For this we must assume that the suboxide has a density approximately that of UO_2. This is plausible in terms of the lattice parameters ordinarily assigned to UO(?)(4) or other postulated suboxides.(5) Then in terms of the specific volumes

$$2\ UO \rightarrow U + UO_2$$

$$2(0.09) \rightarrow 1(0.05) + 1(0.09)$$

$$0.18 \rightarrow 0.14 \text{ (reduction of 0.04 in specific volume)}$$

The volume shrinkage is approximately equal to the volume of uranium produced.