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PREPARATION OF REACTOR-GRADE UO_2 FROM UO_3 BY ARC FUSION

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PREPARATION OF REACTOR-GRADE UO_2 FROM UO_3 BY ARC FUSION

by

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August 1968

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ABSTRACT

An arc-fusion process was developed that converts UO_3 to reactor-grade UO_2. UO_3 is fed to a carbon-arc furnace with internally insulated walls that maintain the temperature of the entire charge above the decomposition temperature of UO_3 ($\sim$650°C), and thereby eliminate diffusion of oxygen from UO_3 at the walls to product nearer the center.

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INTRODUCTION

A major production cycle at the Savannah River Plant (SRP) uses fuel elements made from natural or slightly enriched uranium metal. After irradiation, these elements are dissolved and the plutonium and uranium are separated from fission products. The recovered depleted uranium is converted to UO_3, and is stored in warehouses.

Recycle of this uranium within the Savannah River Plant was believed, at the time of this study, to offer cost savings and increased flexibility of production. Since the UO_3 produced is not sufficiently stable for irradiation, it must be converted to a lower oxide such as U_3O_8 or UO_2 to give satisfactory operation in a reactor. In this mode of recycle, uranyl nitrate solution from SRP would be "sweetened" slightly in ^{235}U before denitration to UO_3, the UO_3 would be converted to reactor-grade UO_2 (high density, low gas and impurity content), and the UO_2 would be fabricated into fuel elements by vibratory compaction.

Reactor-grade UO_2 has been produced from UO_3 commercially by several processes.[1]

- High-fired UO_2 produced from milled UO_2 powder: Reduction of UO_3 to UO_2 in a hydrogen atmosphere, pulverizing to ~1 micron, production of "green" pellets using a binding agent, and sintering in a CO_2 atmosphere followed by firing at 1700°C in a hydrogen atmosphere.
- High-fired UO_2 produced from ammonium diuranate (ADU): Same as above, except the fine UO_2 powder is formed by ADU precipitation from uranium hexafluoride.
- Arc fusion of "light" UO_2 to dense UO_2 by melting in an electric-arc furnace.[2]

A variety of other methods, including variations of the first two above, have been studied on an experimental scale, but none has been put into large-scale plant practice in the United States. Experimental work of a scouting nature was done at the Savannah River Laboratory (SRL) on three alternative processes aimed primarily at low capital expenditures.

- Reduction and sintering of pelletized UO_3 with hydrogen in a resistance furnace.[3]
- Decomposition and sintering of large-granule UO_3 in an induction furnace.
- Decomposition and fusion of UO_3 with a plasma-arc or carbon-arc, skull-melting technique.

Preliminary experimental work on the first two processes indicated potential problems in obtaining the desired density, whereas the work with a carbon arc was encouraging. Therefore, a program was undertaken at SRL to develop a process for direct conversion of UO_3 to reactor-grade UO_2 by carbon-arc fusion. The results of the program are summarized in this report.

SUMMARY

An arc-fusion process was developed that converts UO_3 to reactor-grade UO_2 with an O/U ratio between 2.00 and 2.05, a particle density >95% of theoretical, and impurity contents of <100 ppm N_2 and <100 ppm carbon. UO_3 is fed to a carbon-arc furnace with internally insulated walls that maintain the temperature of the entire charge above the decomposition temperature of UO_3 (~650°C), and so eliminate diffusion of oxygen from UO_3 at the walls to product nearer the center. Both melting and cooling are done under a flowing blanket of argon, as still another measure to control oxygen and nitrogen content of the product. UO_3 powder is continuously added to the furnace by a screw feeder as fusion occurs; the product is removed as a batch after cooling. Temperatures in excess of 2850°C, the melting point of UO_2, are attained during the heating period.

DISCUSSION

PRIOR KNOWLEDGE

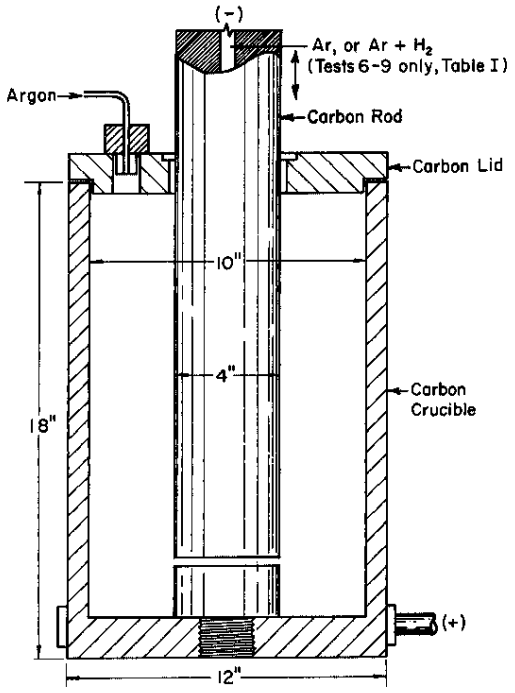
Nonreactor-grade UO_2 or U_3O_8 is fused by carbon arcs in water-cooled steel vessels by the Norton Company[2] after UO_3 is reduced to the nonreactor-grade oxides in a separate facility. The UO_3 or U_3O_8 is fed into the vessels continuously, and the carbon electrodes are withdrawn as the liquid level rises. After the charge has been melted and allowed to cool, the product is removed as a central mass of fused material with a "skull" of unmelted material at the wall. The Norton Company was recently granted a patent[4] on their process for making reactor-grade UO_2 by using a gas purge through the oxide during cooling to control impurities and stoichiometry.*

DESCRIPTION OF EQUIPMENT

10-Inch Carbon-Arc Furnace

A 10-inch (ID) carbon-arc furnace with a 4-inch diameter electrode (Figure 1) was built entirely of carbon, with no special provision for cooling the crucible. The carbon pot itself was used as the anode; the carbon rod, as cathode. Power was supplied by a 40-kw, 55-volt DC welding machine. The rod was held stationary while the carbon pot was moved up and down with a scissors jack. A "blanket gas" line was also provided. The unit was later modified for addition of feed during a test.

* When SRL began this study on direct conversion of UO_3 to reactor-grade UO_2, the Norton Company was not in a position to reveal their proprietary information; so much of the process had to be developed independently.



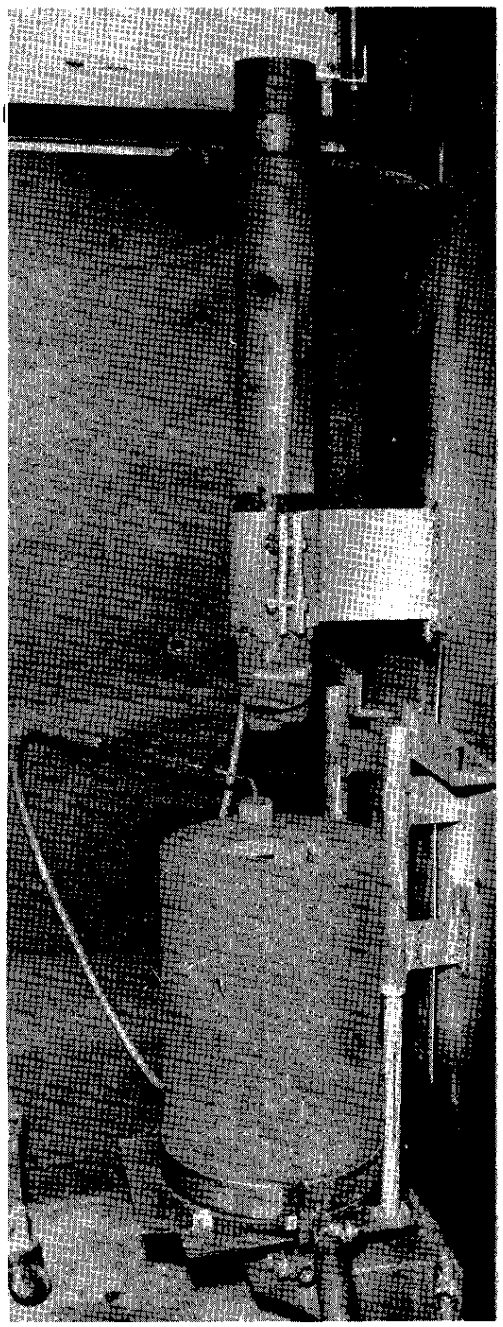
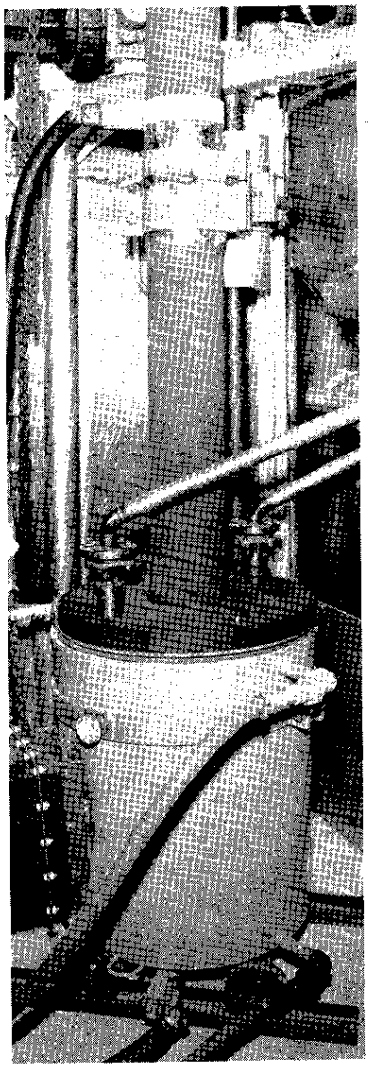


FIG. 1 10-INCH CARBON-ARC FURNACE

18-inch Carbon-Arc Furnace

In order to produce large batches of material and to obtain operating experience with equipment more suitable for plant operation, an arc furnace with an 18-inch-diameter steel crucible, a 6-inch-diameter movable electrode (initially), and an 80-kw power supply was fabricated (Figure 2). The steel crucible was surrounded by a water jacket, and had a stationary, but replaceable, carbon electrode projecting through the bottom. The movable electrode was positioned by a motor-driven screw. A vibrator was attached to the crucible to assist in moving the feed into the melt zone. The unit was later modified to use an 8-inch movable electrode.



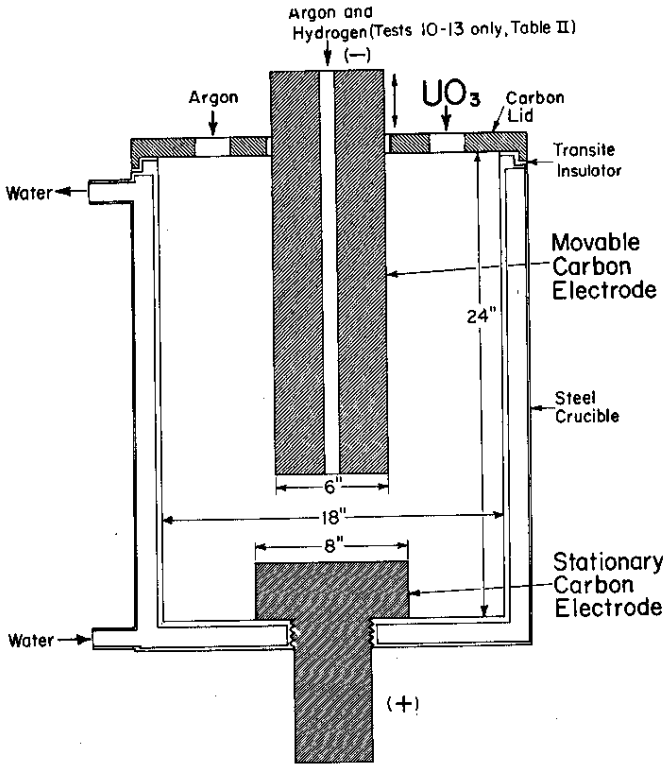


FIG. 2 18-INCH CARBON-ARC FURNACE

TEST PROCEDURES AND RESULTS

10–Inch Carbon–Arc Furnace

Mode of Operation

In a typical fusion test, the crucible was raised until it touched the carbon rod, and was then filled with uranium oxide powder. Power was applied to the furnace, and the spacing between the carbon rod and the carbon crucible or melt surface (depending on condition of crucible contents) was adjusted to maintain the current at the 800-ampere capacity of the welding machine; the potential at this current was ~50 volts. Argon at 15 scfh was fed into the top of the furnace to exclude air.

Approximately one-half hour after a typical test was started, the top half of the furnace would glow at ~800°C, and a carbon monoxide flame issued from the annulus between the electrode and lid. The portion of the interior that was visible through an optical pyrometer sighted between the carbon rod and the carbon lid was at 1200 to 1400°C. When the electrode was withdrawn at the end of the test, the original full charge of granules had shrunk and the arc was no longer insulated thermally. The insulative layer apparently had been lost after one-half hour of operation, corresponding to glowing of the upper part of the vessel. Therefore, the furnace was modified to allow the addition of uranium oxide powder during fusion in order to maintain an insulating layer at the top surface of the melt.

Effect of O/U Ratio on N_2 Content

Nine arc-fusion tests were made in the 10-inch furnace: two with crushed $UO_{2.00}$ feed of ~88% theoretical density and seven with UO_3 prepared at SRP. Two of the UO_3 tests were made with an argon purge down the center of the electrode during the fusion, and a hydrogen-argon purge through the electrode during the cooling period. Two UO_3 tests were made with no purge during fusion, but with the hydrogen-argon purge through the electrode during cooling. The results of all the tests, summarized in Table I, show that when the O/U ratio of the product is slightly greater than 2.00, the nitrogen content is acceptably low (<50 ppm), but when

TABLE I

Arc-Fused Uranium Oxide in 10-Inch Furnace[a]

Test	Starting Material		Purge Gas Flow, scfh				Fusion, min	Product				
			To Pot		To Electrode			Mass, lb	O/U Ratio	Nitrogen, ppm		Carbon, ppm
	Feed	Nitrogen, ppm	Fusion	Cooling	Fusion	Cooling				Kjeldahl	Pt Fusion[b]	
1	$UO_{2.00}$	20-70	15 Ar	15 Ar	None	None	60	25	1.91	840	-	<25
2	$UO_{2.00}$	20-70	15 Ar	15 Ar	None	None	120	10	1.91	820	-	<25
3	UO_3	↑	15 Ar	15 Ar	None	None	30	35	1.99	210	-	<25
4	UO_3	|	15 Ar	15 Ar	None	None	60	50	2.04	15	-	<25
5	UO_3	|	15 Ar	15 Ar	None	None	60	75	2.12	<20	-	<25
6	UO_3	5,000 to 10,000	15 Ar	15 Ar	15 Ar	29 Ar, 1.2 H_2	20	50	2.11	-	-	-
7	UO_3	|	15 Ar	15 Ar	15 Ar	29 Ar, 1.2 H_2	85	100	2.10	<10	30	155
8	UO_3	|	15 Ar	15 Ar	None	29 Ar, 1.2 H_2	210	71	2.05	<10	50	70
9	UO_3	↓	15 Ar	33 Ar	None	14 Ar, 3.0 H_2	205	25	1.95	510	660	185

a UO_3 feed added during fusion starting with Test 5.

b Analytical technique reported in Reference 5, which includes both absorbed and combined nitrogen.

the ratio is slightly less than 2.00, the nitrogen content is high (up to 650 ppm). The latter relationship holds even when UO_2 with low nitrogen content is used as the feed material. Apparently, substoichiometric UO_2 picks up nitrogen to fill available sites in the oxygen-deficient uranium.

Low Density UO_2

Two tests (6 and 7) made with argon (added through the electrode during the fusion) produced material that was porous and would not meet density specifications (>95% of theoretical); a column of unfired material was observed in the center of the ingot, apparently the result of cooling by the argon.

Photographs of typical UO_2 product are shown in Figure 3, and a cross section of a typical product charge in place in the furnace is shown in Figure 4.

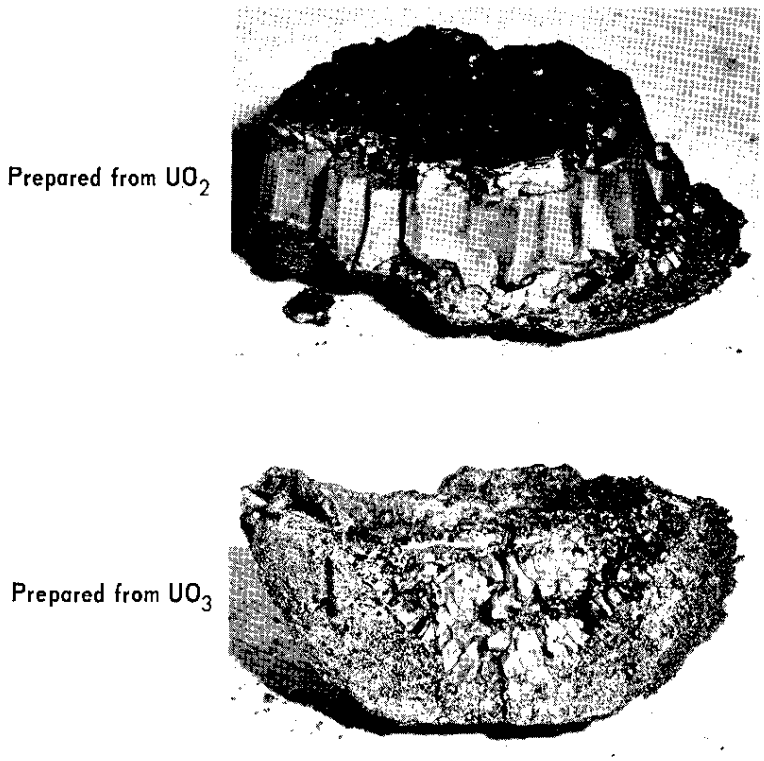


FIG. 3 UO_2 PRODUCED IN 10-INCH FURNACE

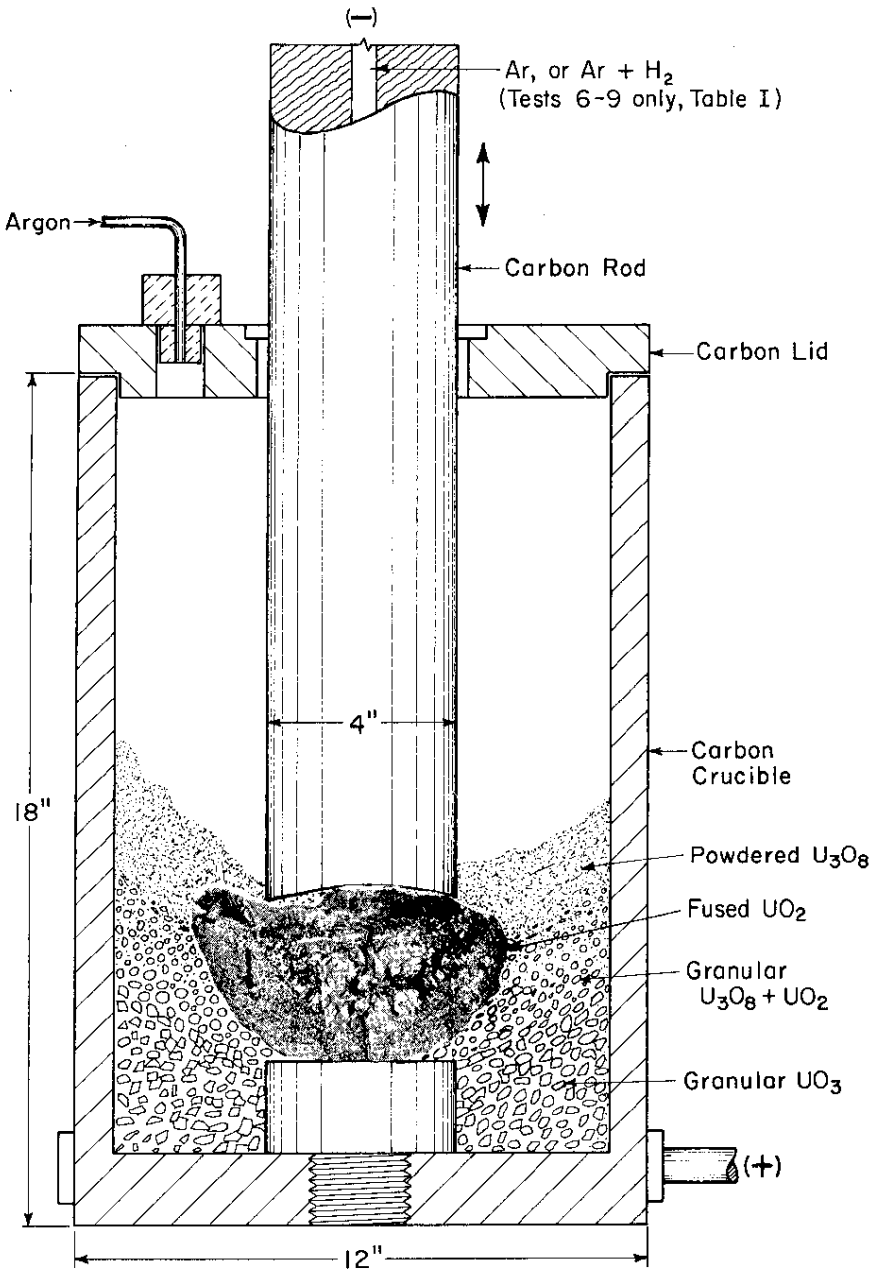


FIG. 4 TYPICAL PRODUCT CHARGE IN 10-INCH FURNACE

18–Inch Carbon–Arc Furnace

Mode of Operation

Operation of the 18-inch furnace was basically the same as for the 10-inch furnace except that for each run the crucible initially contained uranium to a level only ~1 inch above the top of the stationary electrode. The current was maintained at 1000 amperes (limited by current carrying capacity of electrical connections) by adjusting the distance between the end of the movable electrode and the fixed electrode of melt. The feed rate of fresh oxide and the input power were controlled to maintain temperatures of 1100 to 1400°C at the top part of the furnace (measured by sighting through a hole in the furnace top with an optical pyrometer); temperatures above 1400°C at the top of the furnace resulted in rapid deterioration of the carbon lid and excessive electrode consumption. The temperature of the melt exceeded 2850°C.

During the initial part of each test the unit was operated at low feed rates (30% of feeder capacity) and full power (~70 kw), while near the end of the fusion the power had to be reduced to (~50 kw) even at maximum feed rate. The energy consumed in the actual reduction reaction is small; the energy required for heating is reduced as the quantity of material in the furnace increases and acts as an insulator. Typical feed rates and power requirements are shown in Figure 5. Inspection of the furnace after operating for 3 hours showed negligible product, indicating that until the furnace contains appreciable hot oxide no product is formed.

Effect of Temperature on O/U Ratio

The data obtained from nine tests in the 18-inch furnace are summarized in Table II. The product from each of the first three tests was unacceptably high in oxygen (O/U from 2.09 to 2.20), even though a reducing atmosphere was maintained in the furnace during cooling. The high ratio of oxygen to uranium was attributed to diffusion of oxygen, during the cooling period, from

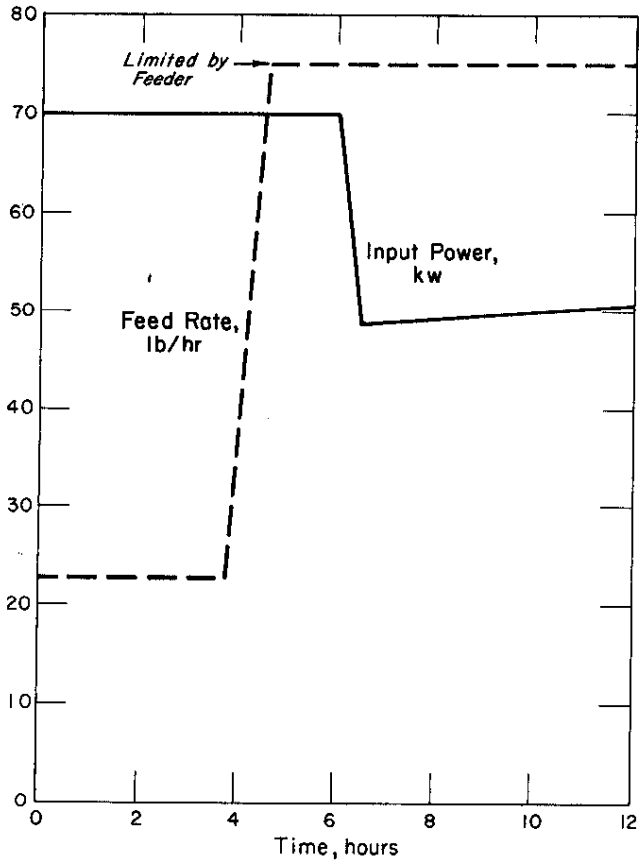


FIG. 5 TYPICAL INPUT POWER AND FEED RATE DURING ARC FUSION OF UO_3 IN 18-INCH FURNACE

undecomposed UO_3 found near the cold furnace walls to the relatively hot UO_2. Justification for this interpretation was found in the fact that lower O/U ratios were obtained in previous tests made with the uncooled graphite crucible (10-inch furnace) for which wall temperatures were at least 500°C. One test in the 18-inch furnace, which was stopped early because of equipment malfunction, had little UO_3 present and also had a low O/U ratio (1.98 and 2.01).

The foregoing evidence indicated that maintaining the temperature in the crucible above the decomposition temperature of UO_3 ($UO_3 \xrightarrow{650\,^\circ C} U_2O_8 \xrightarrow{1125\,^\circ C} UO_2$) eliminates oxygen that can combine with the product during extended cooling periods. Consequently, an insu-

TABLE II

Arc-Fused Uranium Oxide in 18-Inch Furnace

Test	Equipment	Purge Gas Flow, scfh To Pot Fusion	Purge Gas Flow, scfh To Pot Cooling	Purge Gas Flow, scfh To Electrode Cooling	Product[a] Weight, lb	Product[a] O/U Ratio	Product[a] Nitrogen, ppm Pt Fusion[b]	Product[a] Carbon, ppm
10	Cold Wall, 6" Movable Electrode, Manual Feed	15 Ar	32 Ar	14 Ar, 4.0 H_2	105	2.13 2.09	30 10	85 70
11	"	15 Ar	None	46 Ar, 4.0 H_2	115	2.19 2.11	50 20	80 100
12	"	15 Ar	32 Ar	14 Ar, 4.0 H_2	180	2.12 2.15 2.20	55 40 65	80 80 130
13	Insulated Wall, 8" Movable Electrode, Manual Feed	17 Ar	32 Ar	14 Ar, 4.0 H_2	130	2.04 2.05 2.02	40 30 50	25 30 -
14	Insulated Wall, 8" Movable Electrode, Screw Feeder, Gas Purge Tube To Bottom	17 Ar	17 Ar	14 Ar, 4.0 H_2[c]	160	1.93[d] 1.99[e] 2.02[f]	1000 690 40	100 800 840
15	Insulated Wall, 8" Movable Electrode, Screw Feeder	17 Ar	45 Ar	None	280	2.05	10	40
16	"	17 Ar	38 Ar	None	150	2.01	80	90
17	"	17 Ar	34 Ar	None	340	2.02	230	120
18	"	17 Ar	34 Ar	None	245	2.03	35	35

a Analyses of Tests 14, 15, 16, 17, and 18 were on a crushed and blended composite sample; other analyses were made on grab samples.

b Analytical technique reported in Reference 5 which includes both absorbed and combined nitrogen.

c Hydrogen-argon purge in bottom of crucible instead of through electrode (see text).

d Average of analyses before crushing and blending.

e Analysis of material after crushing and blending.

f Analysis made ~8 weeks after e.

lating liner of 1/4 inch "Kaowool"* impregnated with "Astroceram"** or "Glasrock Slurry"*** was installed on the inside of the furnace to ensure a high enough temperature to decompose all of the UO_3. At the same time, the movable electrode diameter was increased to 8 inches to lessen the frequency of replacement, the fixed electrode was increased to 12 inches, and a screw feeder was installed to

* Trademark of Babcock and Wilcox Company for alumina-silica ceramic insulation.

** Trademark of American Thermocatalytic Corporation for high temperature cement.

*** Trademark of Glasrock Products Corporation for high temperature silica cement.

provide a more reliable and uniform rate of addition of UO_3. A cross section of the modified furnace with typical charge is shown in Figure 6.

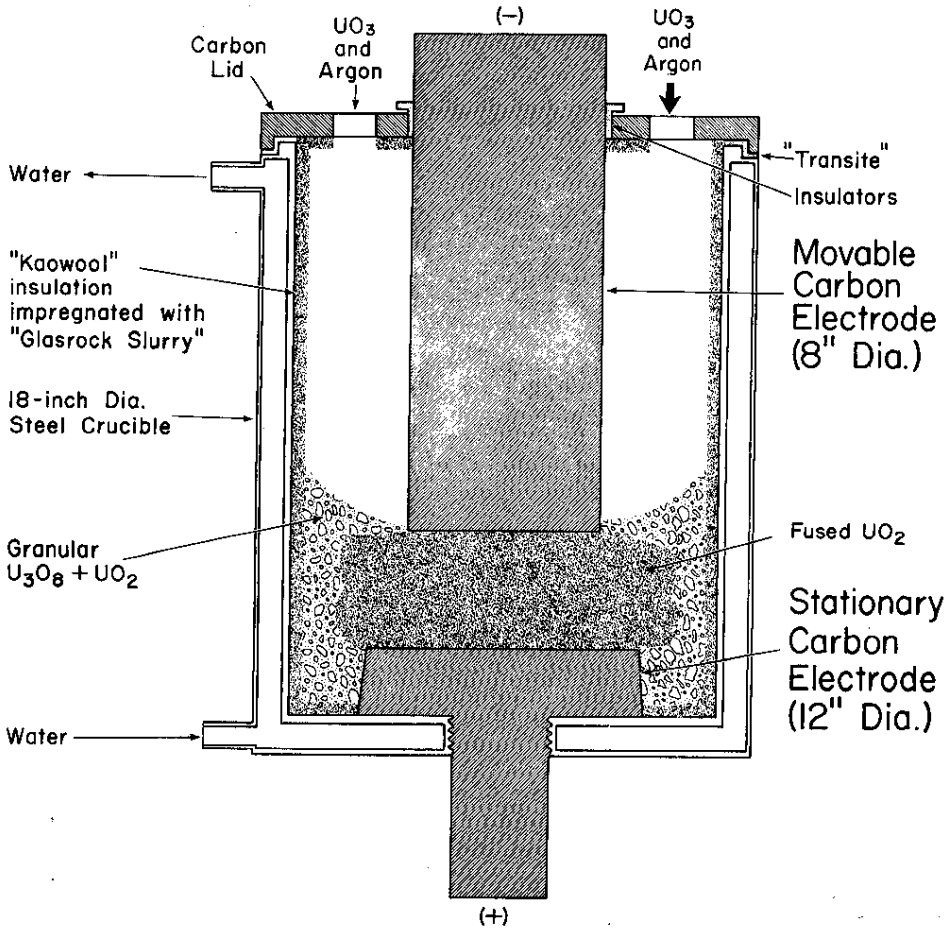


FIG. 6 TYPICAL PRODUCT CHARGE IN INSULATED 18-INCH FURNACE

Obtaining Reactor-Grade UO_2

Four tests were made in the modified furnace using either purified argon (15, 16, 17) or argon-hydrogen (13) as a purge to prevent entry of air. Three of these tests (13, 15, 16) produced reactor-grade UO_2: an O/U ratio between 2.00 and 2.05, a particle density >95% of theoretical, and impurities of <100 ppm N_2 and <100 ppm C. The product from Test 17 was high in nitrogen (230 ppm) even though the O/U ratio (2.02) was greater than 2.00: this contradicted previous data on nitrogen content versus O/U ratio. The only detectable difference between this run and the others was that the UO_3 feed was considerably older (produced 1/64 versus 12/65 and 8/66); the older feed may have had some additive, e.g., $SO_4^=$, which affected its characteristics. A final test (18) made with UO_3 feed representative of recent plant production (produced 9/67) also resulted in reactor-grade UO_2. No additional studies were made to determine the reason for this anomaly. Figure 7 is a photograph of part of a fused ingot made in the 18-inch furnace.

FIG. 7 UO_2 PRODUCED IN 18-INCH FURNACE

Substoichiometric UO_2

Test 14 was made while purging a mixture of 20% H_2 - 80% Ar upward from the bottom of the crucible (the mixture was diluted further with argon before leaving the vessel) during 2 hours of reduced power and no feed, and during the cooling period. Initially the ingot product was low in oxygen (O/U ratio of 1.93) because of the reducing effect of the hydrogen, and the nitrogen content was high (1000 ppm); these results confirmed earlier observations in the 10-inch furnace of the inverse relation between oxygen content and nitrogen content. However, after crushing and blending of the fused ingot, the O/U ratio had increased to 1.99 and the nitrogen content had decreased to 690 ppm (also, surprisingly, the carbon content had increased from 100 to 800 ppm, probably because of accidentally crushing a piece of carbon from the electrode or top cover along with the product). Reanalysis of the crushed and blended sample after exposure to air for several months showed an acceptable O/U ratio (2.01) and nitrogen content (40 ppm), indicating that the oxygen-deficient UO_2 slowly picked up oxygen, and released nitrogen, until an O/U ratio of >2.00 was attained. Therefore, product that has a substoichiometric O/U ratio and high nitrogen content may be usable after crushing and contact with air.

Life of Insulating Liner

The "Astroceram"-"Kaowool" or "Glasrock Slurry"-"Kaowool" liner installed inside the furnace to increase the temperature of the contents has a usable life of only one or two runs before it must be replaced. A cast ceramic liner or a high temperature metal liner backed with "Kaowool" for insulation may be more durable while providing the same temperature control, but tests of more durable liners were not made.

Material Balance

A complete material balance (Table III) indicated that about 50% of the feed to the arc furnace must be recycled. The percent of material recycled should decrease for larger furnaces. About 2% of the UO_2 fed to the furnace was removed as dust through a vent from the hood containing the furnace.

TABLE III

Material Balance for Arc Fusion of UO_2

	Composition			Weight, lb	U, %
	O/U Ratio	Nitrogen, ppm	Carbon, ppm		
Feed	3.0	-	-	685	100
Product	2.02	230	120	342	53
Recycle					
Unfused Material	2.14	297	700	298	45
Dust	2.8	165	1400	12	2

Electrode Consumption

The movable carbon electrode was consumed at a rate of 0.054 lb per lb of uranium oxide in the crucible. This carbon usage rate is about 1.15 times that required to burn the oxygen to CO during the $UO_3 \longrightarrow UO_2$ reduction; the difference is attributed to inleakage of air. The stationary carbon electrode at the bottom of the crucible was not consumed appreciably during the run, since it was quickly covered with hot UO_2 that then carried the electric discharge.

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