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NUCLEAR FUEL RESEARCH FUEL CYCLE DEVELOPMENT PROGRAM QUARTERLY PROGRESS REPORT [FOR] APRIL 1 TO JUNE 30, 1960

By
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July 27, 1960

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Olin Mathieson Chemical Corporation
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NUCLEAR FUEL RESEARCH

FUEL CYCLE DEVELOPMENT PROGRAM

QUARTERLY PROGRESS REPORT
APRIL 1 TO JUNE 30, 1960

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SUMMARY

This report presents the progress made by Olin Mathieson Chemical Corporation under Contract No. AT-(30-1)-2374 during the period April 1, to June 30, 1960.

Under Task I work was continued on a UO_2 pellet fabrication process based on inert atmosphere sintering at 1,250°C to 1,300°C.

The development of a two-stage sintering method, consisting of a nitrogen soak to densify the non-stoichiometric oxide followed by a hydrogen soak to remove excess oxygen, was initiated. With Davison ADU oxide Lot O, uniform stoichiometric pellets were obtained having a density of 98% of theoretical after 3 hours in nitrogen and 1 hour in hydrogen at 1,250°C. Further progress on this sintering technique, however, was hampered by the fact that the other ADU oxide lots employed in the investigation exhibited relatively poor sinterability. Among these was a small batch ordered for a pilot run prior to the procurement of enriched oxide which was to be prepared under similar conditions for the irradiation testing program. A study of the physical and chemical characteristics of the ADU oxide lots on hand was then begun with the objective of establishing a specification based on the correlation of low temperature sinterability in nitrogen with pertinent properties.

With the aim of producing reactive UO_2 sinterable to high densities, small quantities of non-stoichiometric ADU oxide were prepared in the laboratory. Compacts fabricated from this material were sintered at 1,300°C to densities as high as 10.3 gm/cc by the two-stage method.

A cost study was prepared comparing the low temperature nitrogen sintering process with a conventional high temperature hydrogen sintering process. Based on producing UO_2 pellets of the size used in the Yankee Atomic Reactor, the low temperature nitrogen sintering process is estimated to permit cost savings of $0.025 per pellet.

Under Task II, uranium monocarbide was made in a vertical retort in the following manner: Cleaned and pickled bulk uranium was reacted at 3 psig pressure with deoxidized and dried hydrogen at 250°C in a closed system. The retort temperature was then increased to between 750°C and 800°C and the uranium powder carburized in a purified hydrogen-methane mixture. Variables affecting the carbon content were reaction time and temperature, and the amount of carburizing gas flowed through the retort.

The carbide powders were processed under argon to avoid contamination and burning in air. After compressing at 35 tons per sq. in. pressure and vacuum sintering for one-half hour at 1700°C, the densities varied from 11.30 to 11.71 g/cm^3. Further work is in progress to determine the effect of sintering temperatures between 1700°C and the melting point, the addition of uranium, uranium nitride and uranium oxide, and the addition of selected binding elements, such as niobium and zirconium, on the sintered density of stoichiometric methane produced carbide.

During this report period, the skull furnace was operated systematically to the capacity of the rectifiers to determine design weaknesses and the limitation of the furnace. The preferred charge material was pre-formed uranium carbide made either by melting uranium with graphite in a button furnace or reacting uranium powder with graphite in the solid state to form a pellet. It was found that mold preheat minimized surface imperfections. Casting 5/8 in. diameter by 6 in. long were made in the skull furnace. Work on charge materials, including consumable electrodes, will be continued in the future program.

I. THE DEVELOPMENT OF A LOW COST FABRICATION PROCESS FOR URANIUM OXIDE FUEL (TASK I)

R. B. Holden, N. Fuhrman, L. D. Hower, Jr.

A. Introduction

From the sintering atmosphere study with Davison Lot III oxide, described in the Quarterly Progress Report for January 1 to March 31, 1960 (NYO-2687), it appeared unlikely that an economic low temperature UO_2 pellet production process could be based on single stage sintering in a small fixed concentration of hydrogen. This conclusion resulted from the fact that the concentration of hydrogen had to be minimized at the beginning of the sintering operation so that sufficient excess oxygen could be present to promote densification of the oxide. Since all the excess oxygen should eventually be removed to produce pellets of stoichiometric composition, extended sintering times would probably be required in a large scale operation.

During the reporting period, therefore, an investigation was initiated on an alternate method involving two-stage sintering, first in nitrogen to densify the oxide and next in hydrogen to remove the excess oxygen. The objective of this work was to obtain high density, stoichiometric, uniform pellets in the shortest overall sintering cycle.

B. Process Development Studies

1. Two-Stage Sintering (2-in. Furnace)

The first series of two-stage sintering experiments was conducted in the 2-in. diameter laboratory furnace with the aim of establishing conditions which would lead to a short sintering cycle. Raw oxide from Davison Lot III roasted to yield an initial O/U ratio of 2.27 was used in this work. In each experiment a furnace loading of four green compacts was introduced into the cold furnace and heated in 3 hours under pure nitrogen to the sintering temperature. After a given interval at this temperature, the nitrogen was normally displaced by hydrogen, and the loading was soaked for an additional period before being cooled to room temperature in this atmosphere. The nitrogen and hydrogen flow rates were 2.0 SCFH and 1.7 SCFH, respectively.

The data from these experiments are summarized in Table I-1. Because of the disappointing sintered densities obtained from Sinters 155-158, compacts made from roasted Davison Lot 0, also having an initial O/U ratio of 2.27, were included with Lot III compacts in Sinter No. 159. Previous work with Lot III, reported in NYO-2687, indicated that this oxide was not as sinterable as Lot 0 and confirmation of this fact was again evident from the results of Sinter No. 159. A sintered density of 10.4 gm/cc was obtained for Lot 0, which is 4% higher than the value reported for Lot III in Table I-1.

TABLE I-1

TWO-STAGE SINTERING DATA FOR DAVISON UO_2 (LOT III)

Initial O/U Ratio = 2.27, Sintered in 2-in. Furnace

Sinter Number	Sintering Temp., °C	Soaking Time, Hr. N_2	Soaking Time, Hr. H_2	Linear Shrinkage, %	Geometric Sintered Density gm/cc	Final O/U Ratio
155	1,250	2	-[a]	15.1	9.7	2.00
156	1,250	2	0[b]	14.9	9.8	2.06
157	1,250	2	1	15.0	9.8	2.01
158	1,250	5	1	15.4	9.9	2.01
159	1,300	5	1	15.7	10.0	2.01

a. Compacts soaked in 50% N_2 - 50% H_2 for 2 hours then cooled in N_2.

b. Compacts cooled directly in 100% H_2 without soaking.

Sinters Nos. 155, 156 and 157 included compacts formed at 30 tsi in addition to those formed at the standard 19 tsi. This was done in an attempt to improve the sintered pellet density. All pellets were dimensionally uniform, but each of those formed at 30 tsi exhibited a circumferential crack near the base indicative of an excessive forming pressure. Furthermore, no density improvement was observed. Compacts from the remaining two experiments were all formed at 19 tsi and good dimensional integrity resulted.

From the results of Sinter No. 156, it appears that an elevated temperature soaking period in hydrogen is necessary to effect the complete removal of excess oxygen. Since essentially stoichiometric composition was obtained in Sinters 157-159, it appears that one hour at the sintering temperature is sufficient for this purpose.

It was not possible to establish a near-optimum sintering time and temperature from this work because of the poor sinterability of Lot III; however, the results with Lot 0 in Sinter No. 159 indicate upper bounds for these values, namely, 5 hours and 1,300° C, respectively.

2. Two-Stage Sintering (4-in. Furnace)

Further work on this version of the Inert Atmosphere Sintering Process was carried out in a 4-in. diameter Inconel tube furnace. The primary reason for shifting to this larger furnace was to establish operating conditions for a scale approaching that of production. Moreover, since this furnace has a much larger capacity than the 2-in. furnace, several reference compacts, for example from Lot 0, could be included in the loading as controls.

Experiments were performed with Davison Lot III oxide to arrive at an optimum nitrogen soaking time at 1,250° C. In an attempt to improve the sintering behavior of Lot III, several sinters were also conducted concurrently with oxide which had been subjected to a ball milling pretreatment for 4 hours. Except for this added processing, the green compact fabrication procedure was unchanged from that reported earlier.

The sintering cycle consisted of the following steps: (1) the green compacts in a covered boat were advanced from room temperature to the soaking temperature in one-half hour; (2) they were then sintered in nitrogen for a given period and soaked for an additional hour in hydrogen; (3) when the hydrogen soak was completed, the pellets were removed from the hot zone and cooled for 16 hours (overnight) in a hydrogen atmosphere; (4) both gases were passed through the furnace at the rate of 25 SCFH; (5) before their removal from the furnace, the pellets were advanced to the water-cooled section for a period of one-half hour while the tube was purged with nitrogen; (6) the nitrogen was allowed to flow at 5 SCFH for approximately two hours before the furnace was recharged.

Table I-2 summarizes the results of the Lot III sintering experiments in the 4-in. furnace. In Sinter No. 32 using a 3-hour soaking period a pellet density of 10.1 gm/cc was obtained, which is the highest observed to date for Lot III oxide subjected to the standard pretreatment and sintered to produce stoichiometric composition. A similar maximum density was also achieved in the experiments reported in the last quarterly report (NYO-2687) involving a small fixed concentration of hydrogen in the sintering atmosphere. Since, in addition, the 5-hour soaking times reported in Table I-1 did not yield as high a density, it appears that a 3-hour nitrogen soaking period is near optimum for Lot III at 1,250° C.

An examination of the data reveals that wet ball milling improved the density of Lot III oxide when a 3-hour soaking period was employed in Sinters No. 32 and 35-1. However, these relatively high density pellets exhibited poor dimensional integrity as compared with pellets from unmilled Lots O and III oxide which were included as controls. The results shown for Lot III, milled and unmilled, in both runs demonstrate the degree of reproducibility of the experimental method.

It is noteworthy that with only the standard pretreatment a pellet density of 10.7 gm/cc was obtained with Lot O in Sinter No. 32. Under the same conditions, pellets from yet another lot of Davison ADU oxide, Lot IV, were prepared and had a density of only 9.8 gm/cc.

Efforts to eliminate pellet irregularity by modifications of the sintering conditions were carried out in Sinters 38-1 and 39-1. In the former, a 16-hour purge in hydrogen at room temperature was introduced after the 2-hour nitrogen soak and before the 1-hour hydrogen soak. In the latter, the pellets were sintered in an open boat. Although some improvement in dimensional integrity was achieved, the pellet densities obtained were relatively low.

3. Sinterability and Properties of ADU oxide

The results of the above sintering experiments illustrate how development of the Inert Atmosphere Sintering Process is being hampered by large variations in the sinterability of different lots of starting oxide. Lots III and IV of Davison ADU oxide simply are not as sinterable as Lot O from the same supplier. On the other hand, experiments with a given oxide lot yield quite reproducible results.

At this point, it may be worthwhile to review briefly the early work on this project which led to the exclusive use of Davison oxide as a raw material. Initially, ceramic grade oxides from four different suppliers (Davison, Mallinckrodt, Spencer and Shattuck) were studied. A simple green compact fabrication procedure was developed which differs significantly from other UO_2 pellet processes in only one respect: the as-received oxide is subjected to a roasting operation to introduce additional oxygen before granulation. The Davison oxide, now designated as Lot O, was more amenable to the process as compared with Mallinckrodt UO_2 and was considerably more sinterable than the others. It has consistently produced high sintered pellet densities ranging from 10.4 to 10.8 gm/cc, whereas other oxides used in the program have sintered to a maximum of only 10.1 gm/cc without resort to additional pretreatment.

TABLE I-2

TWO-STAGE SINTERING DATA FOR DAVISON ADU OXIDE SINTERED IN 4-IN. FURNACE AT 1,250° C

Sinter Number	Lot No.	Oxide Pretreatment	Initial O/U Ratio	Soaking Time in N_2, Hr.	Geometric Sintered Density gm/cc	Pellet Appearance
29	III	Dry Ball Milled & Roasted	2.26	2	9.7	Concave top and bottom
30	III	Roasted & Wet Ball Milled	2.36	2	10.0	" " " "
31	III	" " " " "	2.36	1	9.7	" " " "
32	III	" " " " "	2.36	3	10.4	" " " "
32	III	Roasted Only	2.27	3	10.1	Uniform
32	0	" "	2.37	3	10.7	"
32	IV	" "	2.35	3	9.8	"
35-1	III	Roasted & Wet Ball Milled	2.36	3	10.4	Hourglassed
35-1	III	Roasted Only	2.27	3	10.0	Uniform
38-1[a]	III	Roasted & Wet Ball Milled	2.36	2	9.7	Hourglassed
39-1[b]	III	" " " " "	2.36	2	10.0	"

a. 16-hr. H_2 purge at room temperature after N_2 soak.

b. Open boat sinter.

A critical juncture in the project was reached during this quarter when enriched UO_2 for the planned irradiation program was to be procured. Because of the variability problem, a 3 kg pilot batch of depleted Davison ADU oxide (Lot V), prepared on a small scale, was obtained and tested so that the probable sinterability of a specifically enriched ADU oxide batch made under the same conditions could be ascertained. This material was roasted to give an initial O/U ratio of 2.30. The highest pellet density obtained was only 9.5 gm/cc after sintering at 1,300°C in nitrogen for 2 hours followed by soaking in hydrogen for one hour.

A new area of investigation was then embarked upon consisting of a study of the physical and chemical characteristics of the oxide lots on hand to uncover, if possible, the cause of poor low temperature sinterability in nitrogen. The ultimate objective of the characterization would be to correlate the properties with sinterability, so that a raw material specification could be established acceptable to the suppliers. The physical property data determined to date are shown in Table I-3. All the Davison lots contain depleted uranium and were prepared from UF_6. The Numec Lot I contains natural uranium and was produced from uranyl nitrate. An examination of the table reveals no obvious differences that could be related to variable sinterability. More significant data is expected from physical measurements in the following areas which are now under way or planned: sub-sieve particle size analysis, surface area measurements, and optical and electron microscopy. Samples from each lot are also being subjected to chemical analysis for trace constituents, such as fluorine, which could affect sinterability.

The determination of particle size distribution in the sub-sieve range employs ASTM Designation D 422-54T, "Tentative Method for Grain Size Analysis of Soils." The method is based on sedimentation rate and the applicability of Stokes' Law. Preliminary results show a significant difference in the sub-sieve distribution of Lot 0 as compared with that of Lot IV. In Lot 0, 80 wt. % of the particles are below 4 microns in equivalent spherical diameter, with 70 wt. % lying in the 2.5 to 4.0 micron range. In Lot IV, on the other hand, only 6 wt. % of the particles are less than 4 microns in equivalent spherical diameter.

A chemical property which has been reported in the past is the oxidation rate of the oxide. This information is primarily developed to arrive at a suitable roasting schedule for the raw oxide. However, the oxidation behavior of the raw material may be indicative of its sinterability. It is noteworthy that of all the Davison oxides studied in this program Lot 0 exhibits by far the highest oxidation rate as well as superior sinterability. Oxidation rate curves for two recently received Davison oxides, Lots IV and V, are shown in Figures I-1 and I-2, respectively. A comparison of these with such curves for Lot 0, presented in the First Quarterly Progress Report, NYO-2684, clearly demonstrates this difference in reactivity.

TABLE I-3

PHYSICAL PROPERTIES OF AS RECEIVED ADU UO_2

	Lot O	Lot III	Lot IV	Lot V	Numec Lot I
O/U Ratio	2.09	2.05	2.08	2.09	2.10
Moisture, %	0.03	0.08	0.08	0.43	0.44
Sieve Analysis (dry), %					
+20 Mesh	1.5	1.0	0.1	0	0
-20 +40	5.9	7.0	8.6	0.6	5.9
-40 +60	20.6	22.8	12.1	3.5	0.4
-60 +100	26.1	20.8	17.2	16.9	0.7
-100 +200	18.0	24.5	24.5	22.6	6.2
-200 +325	6.5	11.6	15.8	28.3	11.6
-325	21.4	12.3	21.7	28.1	75.2
Wet Sieve Analysis % through 200 Mesh	80.7	85.3	61.5	87.1	94.2
Bulk Density, gm/cc	1.72	1.79	2.12	1.80	1.76

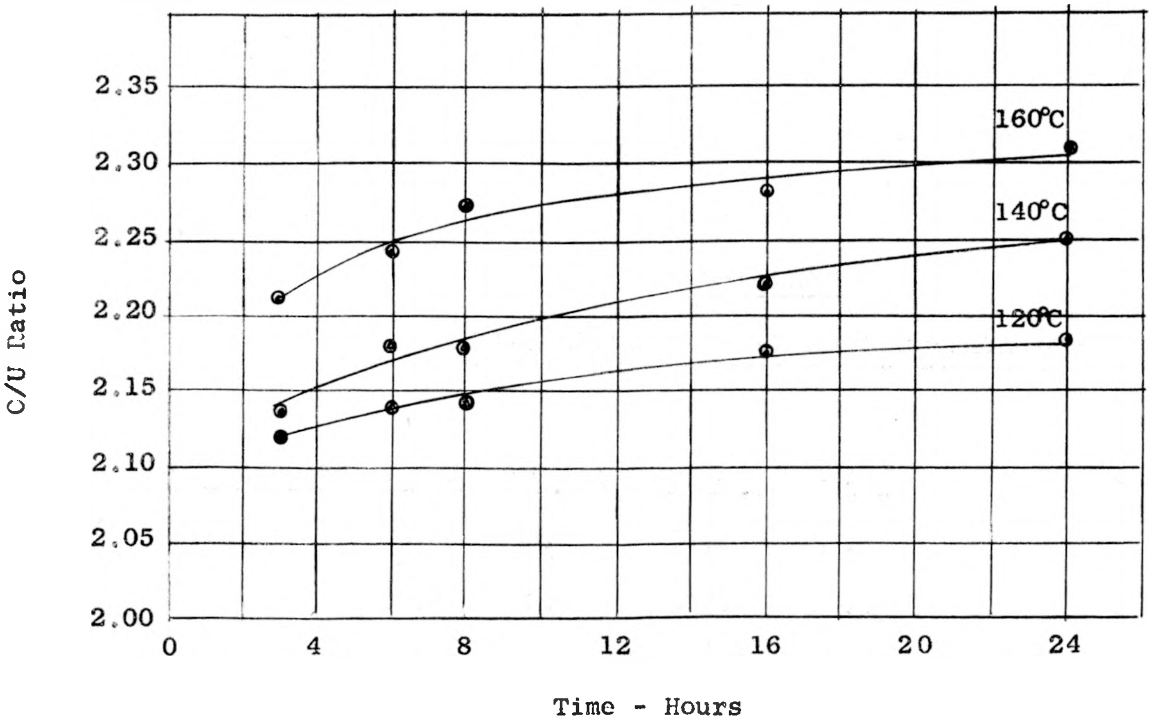

Fig. I-1. Oxidation Rate of Davison Oxide Lot IV as a Function of Time and Temperature

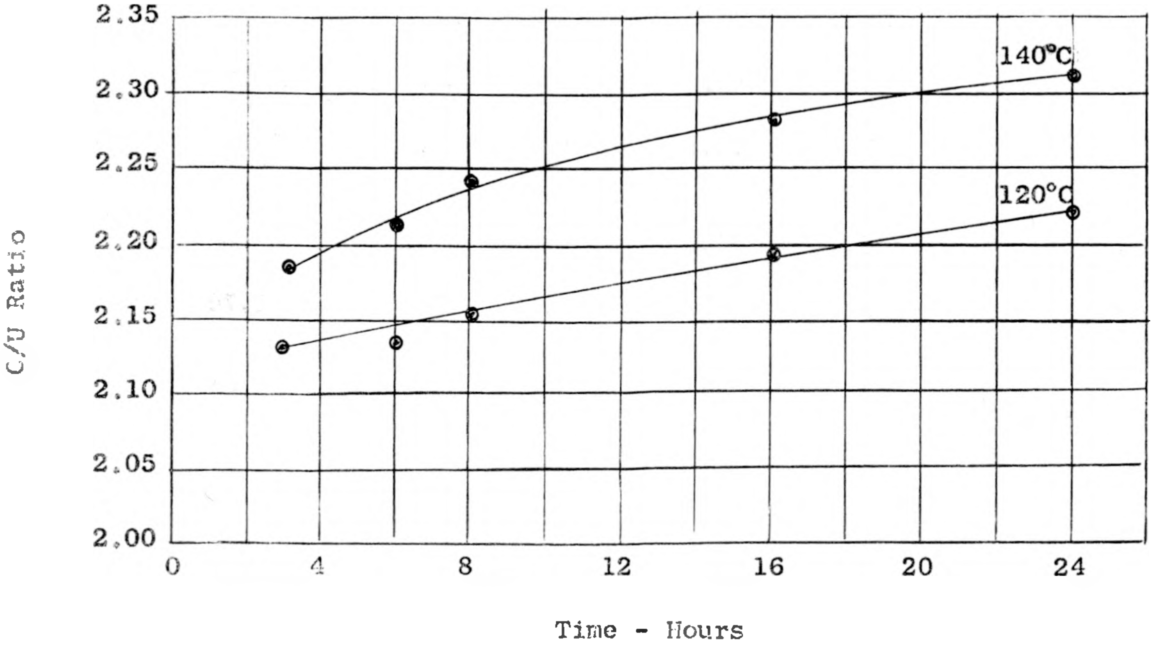

Fig. I-2. Oxidation Rate of Davison Oxide Lot V as a Function of Time and Temperature

Another ADU oxide property which, heretofore, has not been determined in this project is the high temperature sinterability in hydrogen. This property should be meaningful to the oxide producers and would necessarily be an important part of a raw material specification. The first high temperature hydrogen sinter was performed with "as received" Davison Lots 0 and IV and Numec Lot I. The pellets were soaked in hydrogen at 1,650° C for 6 hours in a molybdenum-wound furnace. The following data were obtained:

Oxide	Initial O/U Ratio	Linear Shrinkage, %	Geometric Sintered Density, gm/cc
Davison Lot 0	2.09	19.6	10.6
Davison Lot IV	2.09	17.0	10.0
Numec Lot I	2.10	17.2	9.8

The Davison oxide results are similar to those invariably observed in the low temperature Inert Atmosphere Sintering Process. The poor density of the pellets from Numec Lot I suggests that this material will also not sinter well at low temperatures.

4. Laboratory Scale ADU Oxide Preparation

Because of the ADU oxide variability problem encountered with the suppliers, several small laboratory scale batches of ADU oxide (100-200 gm as UO_2) were prepared toward the end of the quarter with the aim of producing reactive material sinterable to high densities. The preparative procedure first involved the precipitation of ammonium diuranate from a uranyl nitrate solution (100 grams U/liter) with a 15 wt. % NH_4OH solution. The uranyl nitrate was initially heated to 60° C and excess NH_4OH was added to increase the pH to 8. The ADU was separated by filtration, washed with water and oven dried at 100° C.

Each ADU batch was subjected to a number of different pyrolysis procedures to yield non-stoichiometric oxides whose O/U ratios were determined. The results of two-stage sintering experiments (2 hours in nitrogen followed by 1 hour in hydrogen) at 1,300° C with several such oxides, as prepared, are presented in Table I-4. In some experiments as noted under "Remarks," the resulting oxide was pyrophoric, i. e., spontaneous oxidation was observed at room temperature when it was exposed to air after the reduction step. The uniformity of color reported is indicative of the homogeneity of the oxide with respect to excess oxygen content. The ammonia in the $NH_3 + N_2$ atmosphere referred to in the table was supplied by the decomposition of the ADU in essentially a closed system under nitrogen.

TABLE I-4

EXPERIMENTAL DATA ON LABORATORY PRODUCED ADU OXIDE SINTERED at 1,300°C*

ADU Batch No.	Pyrolysis Schedule	O/U Ratio	Linear Shrinkage, %	Pellet Sintered Density gm/cc	Remarks On Oxide Appearance
2	4 hr. in N_2 @ 750°C	2.18	19.8	10.3	Stable, non-uniform color
3	4 hr. in $NH_3 + N_2$ @ 850°C	2.23	18.1	9.3	" " " "
4	4 hr. in $NH_3 + N_2$ @ 850°C	2.30	20.2	10.0	" " " "
3	5 hr. in 60% H_2 - 40% N_2 @ 850°C	2.32	22.5	10.2	Pyrophoric - green to black
4	5 hr. in 60% H_2 - 40% N_2 @ 850°C	2.15	22.2	10.3	Uniform - brown
3	4 hr. in Air @ 750°C, 2 hr. in 40% H_2 - 60% N_2 @ 850°C	2.04	14.9	9.2	Stable, uniform - olive
4	4 hr. in Air @ 350° C, 4.5 hr. in 93% N_2 - 7% H_2 @ 850°C	2.07	18.9	9.7	" " "
5	4 hr. in Air @ 350°C, 4.5 hr. in 93% N_2 - 7% H_2 @ 850°C	2.05	17.6	9.5	" " "
4	4 hr. in Air @ 360°C, 4.5 hr. in N_2 @ 850°C	2.61	25.0	10.2	Stable, uniform - grey
5	4 hr. in Air @ 360°C, 4.5 hr. in N_2 @ 850°C	2.62	25.6	9.9	" " "
4	4 hr. in Air @ 360°C, 12 hr. in N_2 @ 850°C	2.64	24.1	9.9	" " "
5	4 hr. in Air @ 360°C, 12 hr. in N_2 @ 850°C	2.59	26.1	10.3	" " "
4	12 hr. in N_2 @ 850°C	2.02	10.3	8.2	Stable, uniform - brown
5	12 hr. in N_2 @ 850°C	2.03	9.3	7.5	" " "

***Two-stage sintering: 2 hr. in nitrogen, 1 hr. in hydrogen.**

The data in Table I-4 demonstrate that ADU oxides other than Lot 0 can be sintered to fairly high density with the Inert Atmosphere Sintering Process without resort to special activating treatments such as ball milling. The enhancing effect of excess oxygen on the sinterability of ADU oxide is also shown.

C. Cost Estimates of UO_2 Pellet Production

To properly assess the economic advantage of low temperature sintering, preliminary estimates were prepared for the cost of UO_2 pellet production by (1) the Inert Atmosphere Sintering Process and (2) a conventional high temperature hydrogen sintering process. Both estimates were based on production facilities designed to process 50 tons of UO_2 per year into pellets meeting the Yankee Atomic Electric Company Reactor specifications.

A comparison of the fixed capital and operating cost estimates is summarized in Table I-5. The cost data indicate that the estimated pellet cost of the low temperature process is $0.025 less than that of the high temperature process. A major contributing factor for this difference is the higher initial cost and maintenance cost of the furnaces and accessories, such as boats, required for hydrogen sintering.

D. Conclusions

The problem presented by the ADU oxide variability with respect to sintering characteristics demonstrates the need for a program designed to correlate physical and chemical properties with low temperature inert atmosphere sinterability. In particular, such a program should be concerned with properties which can be controlled by the ceramic grade oxide producers in their various manufacturing processes.

E. Work Plan for the Next Quarter

Work will be continued on the study of the physical and chemical characteristics of the oxide lots on hand. Emphasis will be placed on uncovering the differences between Lot 0 and those ADU oxide lots which have not exhibited similar reactivity. Oxide suppliers will be contacted to determine the acceptability of an oxide specification based on the results of this work.

Although a subcontract for irradiation testing has been signed with the Westinghouse Testing Reactor, tests will not proceed until assurance is obtained that a small lot of enriched ADU oxide procured for this purpose can be sintered to high density by the Inert Atmosphere Sintering Process.

TABLE I-5

COMPARISON OF ESTIMATED COSTS FOR FABRICATION OF UO_2 PELLETS*

Low Temperature Nitrogen Sintering vs. High Temperature Hydrogen Sintering

	High Temp.	Low Temp.
I. Total Fixed Capital	$ 866,000	$ 555,000
II. Operating Cost (per pellet basis)		
A. Direct Labor	$ 0.026	$ 0.020
B. Overhead (100% of Direct Labor)	0.026	0.020
C. Depreciation (20% of Fixed Capital in Equipment)	0.020	0.013
D. Equipment Maintenance	0.008	0.003
E. Materials and Supplies	0.002	0.001
F. Direct Services (Chem. Analysis)	0.028	0.028
Total Operating Cost	$ 0.110	$ 0.085

*Basis: Capacity of 50 tons UO_2 per year meeting Yankee Atomic Electric Company Reactor pellet specifications.

II. THE DEVELOPMENT OF URANIUM CARBIDES AS A NUCLEAR FUEL (Task II)

H. S. Kalish, F. B. Litton, J. Crane, W. C. Hahn

A. Introduction

The technical feasibility of preparing bodies of uranium carbide by both casting and powder metallurgy methods was demonstrated by research reported in the three previous quarterly reports under this project. Work was continued during this period on refining skull furnace design, developing skull melting techniques, and controlling the analysis of uranium monocarbides prepared by the methane reaction.

B. Uranium Monocarbide by the Methane Reaction

It was observed that uranium carbide prepared by reacting uranium powder with tank methane resulted in an inconsistent product analysis as determined by chemical, x-ray and metallographic methods. Refer to report NYO-2688. The product contained low carbon and high oxygen and nitrogen content. While the sintered density was usually near theoretical and the structure was body centered cubic ($a_0 = 4.9417 \pm 0.0002$ Å) for this material, it was obvious that impurities should be minimized and brought under positive control for an acceptable uranium monocarbide product.

It appeared that a major source of contamination was in the extensive handling of both the hydride and carbide powders prior to sintering.

A new retort was constructed in order to transfer the carburized product from the reaction furnace directly to the dry-box without intermediate exposure to atmospheric contamination. The retort was made from a 4-in. diameter Inconel tube equipped with a water-cooled head, thermocouple well, and valved gas inlet and outlet tubes. The uranium stock was supported on a tiered, perforated sheet steel platform. This support was constructed to enable the hydride, as it formed by reacting with the uranium, to fall through the perforations and be distributed on the lower tiers for subsequent carburization. The position of the thermocouple may be adjusted to measure the temperatures of both the hydriding and carburizing zones.

Production of uranium carbide was achieved in the following manner: About one pound of bulk uranium was pickled in nitric acid, rinsed in water, dried with alcohol and immediately placed in the retort. The retort was sealed and flushed with argon; deoxidized and dried hydrogen was flowed through the system for 15 minutes prior to heating. The uranium was hydrided at 250°C in a closed system under a pressure of hydrogen equal to 3 psig. After hydriding, the carburizing gas mixture (18% H_2, 81% CH_4, 0.01% O_2 and 0.6% N_2 by volume) was flowed through the system and the retort temperature raised for carburizing. After reaction, the retort was sealed, cooled, and removed to the dry box for discharging.

The chemical analyses of carbide powder produced at three carburizing temperatures are recorded in Table II-1. These are compared to previously

TABLE II - 1

CHEMICAL ANALYSIS AND SINTERED DENSITIES OF RETORT PRODUCED CARBIDE

Lot No.	Reaction* Temperature, Deg. C	Chemical Composition, Percent Sintered Material Carbon	Oxygen	Nitrogen	g/cm3 Sintered Density
3C-HM-26	800	5.21	0.26	0.11	11.66
3C-HM-29	800	5.13	0.12	0.10	11.30
3C-HM-28	750	4.54	0.17	0.30	11.40
3C-HM-28	750	4.59	0.16	0.23	11.45
3C-HM-27	700	4.40	0.55	0.13	11.41
3C-HM-27	700	4.43	0.22	0.17	11.71

*Two hour reaction time

prepared powders containing 4.16% C, 0.72% O_2 and 0.09% N_2 and 3.15% C, 1.23% O_2 and 0.76% N_2; and having sintered densities of 13.69 and 13.46 g/cm^3 respectively. The data in Table II-1 shows a substantial decrease in oxygen and nitrogen contents and an increase in carbon contents in retort processed uranium monocarbide.

The stoichiometric retort processed carbide powders were compacted in an argon atmosphere at 35 tons/in^2 pressure, and vacuum sintered for one-half hour at 1700°C. This time and temperature was selected because high sintered densities were obtained with powders containing relatively high oxygen and nitrogen contents. While the chemical analysis of retort processed monocarbide was satisfactory, the sintered densities were low, varying from 11.30 to 11.71 g/cm^3. These values are significantly lower than the near theoretical densities obtained on material with higher oxygen and nitrogen contents.

Further work is in process to determine the effect of sintering temperature on the density of stoichiometric monocarbide. Sintering temperatures from 1700°C up to the melting will be investigated. A study of the effect of small additions of uranium, uranium nitride, uranium oxide, niobium and zirconium on the sintered density and structure of stoichiometric carbide is to be started.

C. Arc Melting and Casting Uranium Carbide

The object of work reported in this section was the study of skull melting as a means for consolidating uranium carbide.

1. The Skull Furnace

The skull melting furnace was successfully operated during this period to prepare castings 5/8-in. diameter by 6-in. long. Several minor changes were made in the furnace design while developing carbide melting and casting practice. These were as follows:

a) Tantalum heat shields around the crucible were substituted for stainless steel, due to rapid deterioration of the latter from arc blow and metal spatter from the crucible. A sufficient number of melts were made with the tantalum shields to indicate that this material was satisfactory.

b) The sight ports were shielded with stainless steel screening on the inside to reduce heat and spatter damage to the glass.

c) Early difficulties with melting of the copper adapter used to connect graphite electrodes was eliminated through the use of a water cooled threaded adapter attached directly to the electrode. At the maximum time and current presently used, no heat damage to the holder has been noted since incorporating this change. The graphite electrodes in use are 2-1/2-in diameter by 8-in. long. Smaller diameter electrodes were inadequate.

d) The existing electrode drive mechanism was satisfactory for the present studies, provided the ejection of the electrode and casting are concurrent. However, a more rapid means of removing the electrode is desirable. No change is planned in electrode drive at this time.

e) Cooling coils were installed on the electrode port to reduce excessive heating.

Although the above design changes extended the limit of operation of the skull furnace, inherent arc deflection in the furnace remain a problem at currents above 2000 amperes. Consequently, the amount of material which can be poured is limited to about 500 grams of carbide. This is adequate, however, to meet the objective of the experimental program.

2. Melting Cycle

A melting cycle for casting the carbide was established which permits the pouring of approximately 500 grams of material into the mold and funnel assembly. Cropped castings as presently produced weigh about 300 grams. The melting cycle is essentially as follows:

1000 amperes at 30-35 volts for 1 minute
1500 amperes at 30-35 volts for 1 minute
2000 amperes at 35-40 volts for 2 minutes
2400-3000 amperes at 40 volts for 1 minute

3. Mold Design

Castings were made employing both cold and pre-heated graphite molds. Diameters of 1/2-in. and 5/8-in. with lengths of about 6-in. were used. The larger diameter castings were in the majority.

For the casting experiments employing a mold pre-heat the resistance of the mold and sprue assembly to the passage of a direct current was used as the heating mechanism. The mold assembly is shown in Fig. II-1 and the lay-out of the mold assembly, along with a 5/8-in. by 6-in. casting, is shown in Fig. II-2. The outer graphite cylinder is used for support only and is electrically insulated from the remainder of the assembly by ceramic insulation. Power is provided through a 3-in. diameter graphite bar connected to the sprue at one end and to a water cooled copper tube at the other, entering the furnace chamber through a vacuum seal.

Mold temperatures up to 1370°C have been obtained with molds 5/8-in. in diameter and 3/16-in. walls using a heating current of about 1500 amperes. Sprue temperature of about 870°C result under these conditions. Pre-heat time is of course dependent upon mold wall thickness, for the previously mentioned design about one minute is required to reach the desired temperature, although three minutes are necessary to heat the sprue to 860°C.

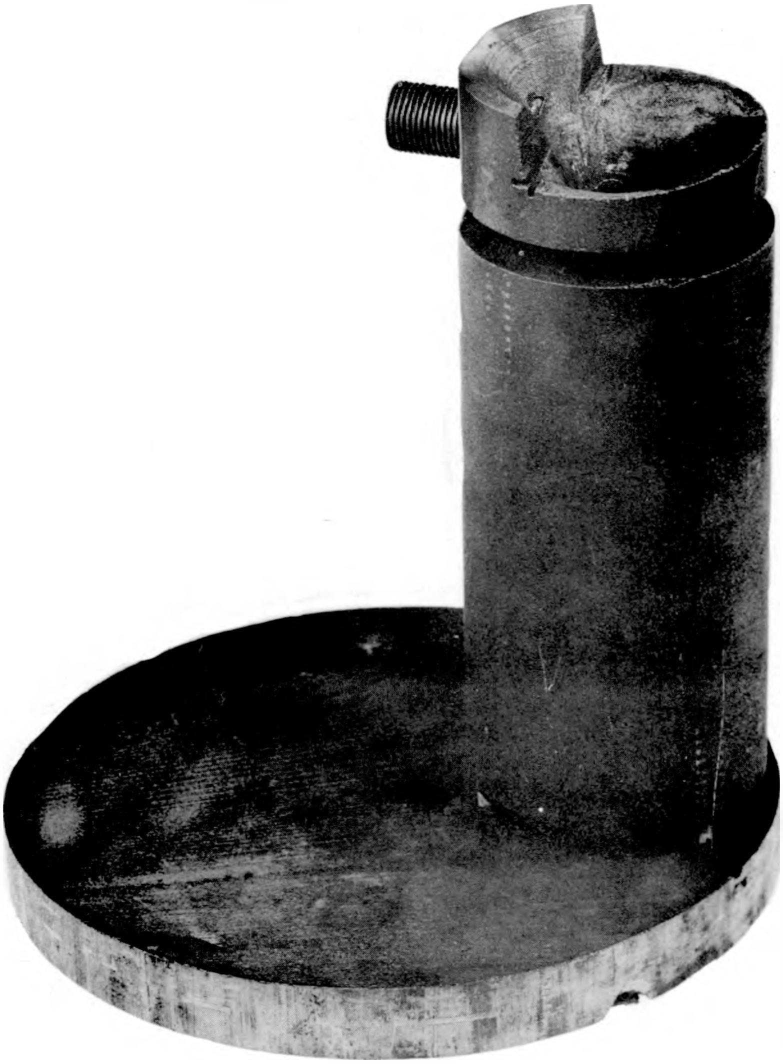

Fig. II-1 Assembled graphite mold for uranium carbide casting - 1/2 actual size.

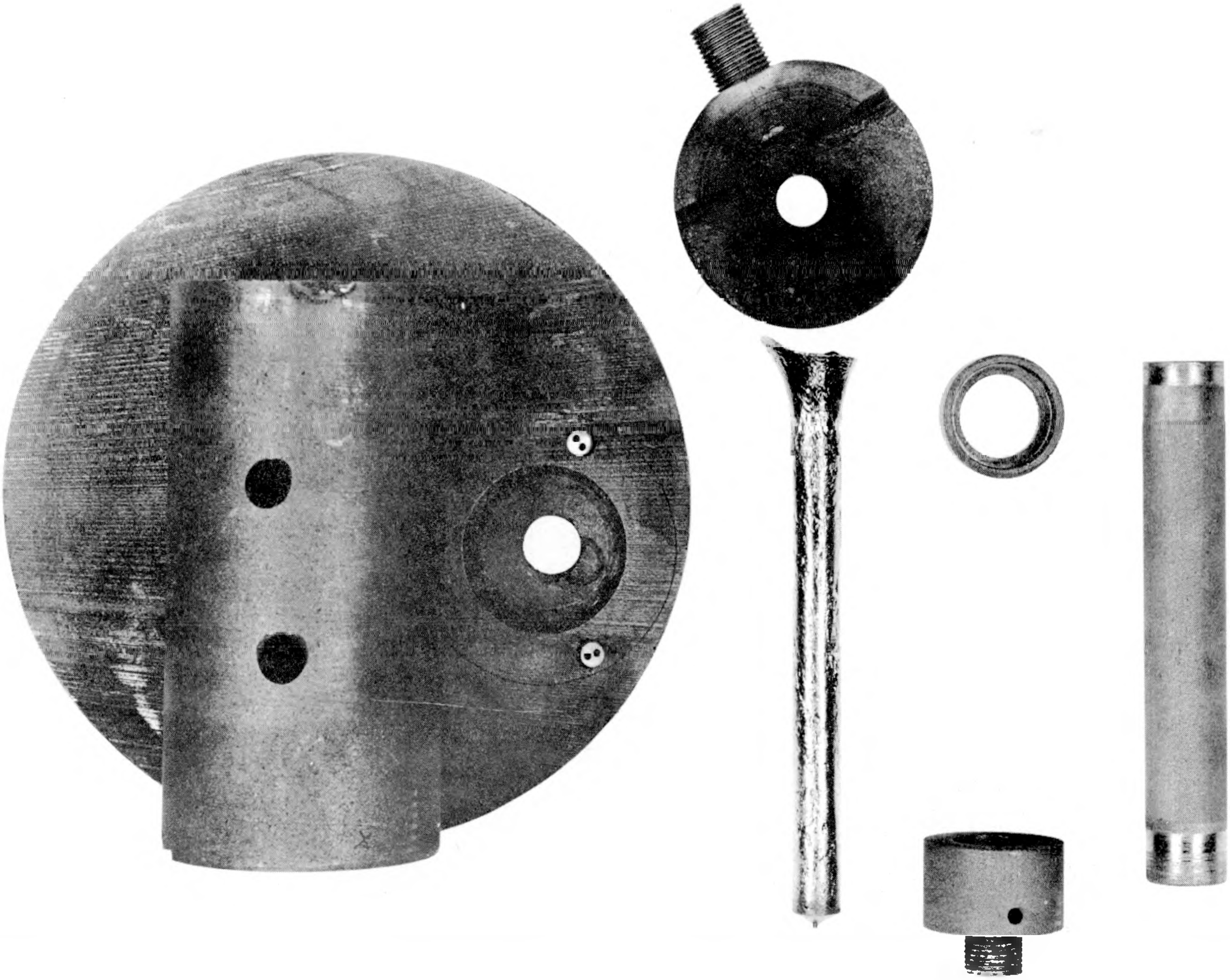

Fig. II-2 - Lay-out of mold assembly showing a 5/8-in. x 6-in. uranium carbide casting.

Right - Graphite mold

Top Center - Sprue and threaded electrical connector

Left - Assembly plate and mold support

- 1/2 actual size.

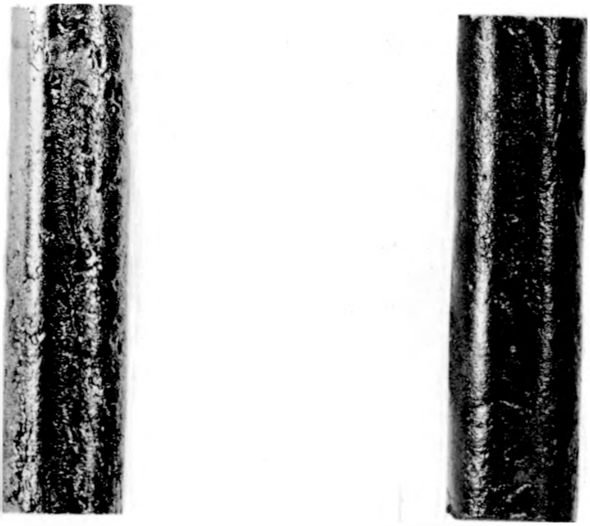

Fig. II-3 Typical view of casting surface made with and without mold pre-heat, left and right respectively - actual size.

4. Castings

With the 5-minute melt cycle described in the previous section, castings were made using cold and pre-heated molds. In general it has been found that a smoother surface is possible using the pre-heated mold, but frequently this surface suffers deterioration by flaking of a thin skin.

Castings made have exhibited one or more of the following defects:

a) Excessive shrinkage - Excessive shrinkage occurs in the top section of the casting as either pipe or shrinkage porosity. Small voids which appear to be secondary pipe have been noted in two castings. There is insufficient evidence to indicate the extent of secondary pipe in these castings.

b) Cracking - Transverse fracture and/or cracking has occurred on all 5/8-in. x 6-in. castings made to date. Branch cracking in the center of the cross-section, but throughout the length of the casting, was noted in one or two recent castings which were metallographically examined.

5. Casting Surface Quality

Flow lines and superficial cold shuts have been far less prevalent on surfaces of castings made using pre-heated molds. Typical surfaces of 5/8-in. diameter castings produced with and without mold pre-heat are shown in Figure II-3.

6. Skull Preparation and Casting Charge

Charge material for skull preparation and casting experiments was introduced into the furnace as uranium metal and graphite pieces, as sintered or pre-sintered uranium carbide pellets and as carbide buttons previously prepared by arc melting. Of these various forms the pre-sintered carbide pellets and the arc melted buttons proved easiest to melt and cast into a homogeneous carbide body. Analytical data are not completed at this time on castings made from these charge materials.

Future work will consist of the development of electrode and/or charge materials for arc melting, including oxide-graphite pre-forms.