MASTER

NYO-2692

NUCLEAR FUEL RESEARCH FUEL CYCLE DEVELOPMENT PROGRAM, QUARTERLY PROGRESS REPORT, JANUARY 1 TO MARCH 31, 1961

May 17, 1961

Olin Mathieson Chemical Corporation
New Haven, Connecticut

UNITED STATES ATOMIC ENERGY COMMISSION • OFFICE OF TECHNICAL INFORMATION

This report has been reproduced directly from the best available copy.

Printed in USA. Price $1.00. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

USAEC Office of Technical Information Extension
Oak Ridge, Tennessee

NYO - 2692
METALS, CERAMICS, AND MATERIALS

NUCLEAR FUEL RESEARCH

FUEL CYCLE DEVELOPMENT PROGRAM

QUARTERLY PROGRESS REPORT

JANUARY 1 TO MARCH 31, 1961

Olin Mathieson Chemical Corporation
New Haven, Connecticut

Date of Issuance: May 17, 1961

Nuclear Fuel Research Laboratory
E. Gordon, Technical Manager
Contract AT(30-1)-2374

Blank Page

CONTENTS

SUMMARY

This report presents the progress made by Olin Mathieson Chemical Corporation under Contract No. AT(30-1)-2374 during the period January 1 to March 31, 1961.

Under Task I, the laboratory scale development phase of a process for the fabrication of UO_2 pellets based on low temperature sintering in nitrogen was essentially completed. Work was initiated on the preparation and encapsulation of enriched UO_2 pellets for irradiation testing.

Further investigation of the effect of fluoride additions on the sintering behavior of UO_2 confirmed that oxidation-reduction cycling restored the oxide sinterability lost as a result of fluoridation. The restoration was accompanied by removal of the fluorine during the activation treatment, and the major portion of this impurity was found to be extracted by the oxidation step. A proposed sintering mechanism for non-stoichiometric UO_2 is discussed in terms of the effect of impurities, such as fluorine, on sinterability.

A series of sintering experiments were performed with the objective of producing high density UO_2 pellets in excess of 98% T.D. Processing conditions, such as forming pressure and sintering schedule, were varied without producing a significant density increase above the normally attained 95% to 97% T.D. range. It was found, however, that modifications of the oxidation-reduction activation treatment could produce densities as high as 98.1% T.D. This was accomplished with ceramic grade oxide subjected to three successive oxidation-reduction cycles and with the same oxide given a single cycle treatment with a prolonged oxidation step of 16 hours duration instead of the usual 1.5 hours.

The results of preliminary sintering experiments with 4.95% enriched UO_2 procured for irradiation indicate that 98% T.D. pellets may be readily prepared for the testing program. It also appears that a sintering temperature as low as 1000°C can be employed to prepare pellets of the design density of 95% T.D. Plans call for the inclusion of both of these pellet types in the irradiation experiments.

Under Task II, the propane reaction was further studied to develop techniques for preparing uranium carbide powder to a given total carbon specification. It was found that stoichiometric uranium monocarbide was obtained by reacting 600 grams of uranium with two liters per minute propane for one-half hour at 600°C. A number of tests were made to determine procedures for reducing the free carbon content. It was observed that the free carbon content of propane produced powder was not affected by either using a copper insert in the retort, diffusion treatment of the powder at relatively low temperature, or the type of charge material used for making the powder.

A comparison was made between the use of unreacted UO_2-graphite and reacted UO_2-graphite charges to the arc skull furnace. The data showed that better control was exercised over the carbon content of the casting through the use of reacted charge material. The material losses involved in the use of unreacted UO_2-graphite made the use of this charge material unattractive. A preliminary cost estimate of uranium carbide castings made from the two types of charge materials was calculated. At three per cent enrichment, the scrap recycling cost placed a severe handicap on the use of unreacted charge material.

The determination of the physical properties of uranium carbide as a function of compositional and fabricational variables was initiated. The thermal expansion of cast 4.85 w/o C uranium carbide was determined at 12.55 x 10^{-6} in./in./°C. No reaction was observed after 100 hours at 800°C between cast 4.8 w/o C uranium carbide and Be, Type 304 stainless steel, Nb, W, Zircaloy-2, Mo, V, Ti and Ta.

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

Work on optimizing the low temperature nitrogen sintering conditions was completed in the previous quarter. This included the establishment of the relationship between pellet density and sintering temperature as well as that between pellet density and initial O/U ratio for several oxide lots. A study of the rate at which excess oxygen is removed from dense oxide pellets by hydrogen was also completed. Essentially all of this work was conducted with ceramic grade oxide which had been activated by oxidation-reduction cycling.

An investigation of the effect of fluoride impurity on the low temperature sinterability of UO_2, initiated in the previous quarter, was continued in this reporting period. As described in the Quarterly Progress Report for October 1 to December 31, 1961 (NYO-2691), it was found that (1) fluoride additions result in the deterioration of sinterability, and (2) oxidation-reduction cycling restores the original activity.

Past development work on this project had been aimed at decreasing sintering time and temperature consistent with the attainment of densities required to meet current fuel specifications. With this objective accomplished, some effort was devoted this quarter to the preparation of very high density oxide (greater than 98% T.D.) based on data previously developed in the program.

The major activity during the quarter, however, was associated with the irradiation testing phase of the project. This included capsule fabrication and the preparation of enriched pellets for encapsulation.

B. Process Development Studies

1. Effect of Fluoride Impurity on UO_2 Sinterability

a. Experimental Results

As discussed in NYO-2691, an investigation of the effect of fluoride impurity on the low temperature sinterability of UO_2 was prompted by the observation that the sintered densities obtained from the as-received Davison oxides exhibited an inverse relationship with fluorine content. The most sinterable, Davison Lot 0, had the lowest fluorine content, and the least sinterable, Davison Lot 5, had the highest fluorine content. It is also worth noting that the physical characteristics of these oxides, such as particle surface area, were found to be quite similar, and the observed difference in sintering behavior could not be explained by any variation in chemical composition other than that of the fluorine content. In initiating this study, the former material was treated with an amount of a dilute HF solution sufficient to increase the fluoride impurity level to a maximum of 3000 ppm. After converting a portion of this fluoridated oxide into pellets by the low temperature nitrogen sintering process, the pellet density was found to be only 8.1 g/cm^3, instead of the usual 10.5 g/cm^3. Another portion of the fluoridated oxide had then been subjected to one standard oxidation-reduction cycle (1-1/2 hours in air at 500°C, followed by 1 hour in hydrogen at 525°C). This material, after processing and sintering under similar conditions, yielded a pellet density of 10.7 g/cm^3.

To establish the role of temperature alone in restoring the activity, a second batch of fluoridated oxide was prepared and a portion heated at 530°C for 2-1/2 hours in nitrogen. Both the fluoridated and the heat-treated materials were processed into pellets for a sinterability evaluation. Again a low pellet density, this time 7.6 g/cm^3, was obtained with the fluoridated oxide. The nitrogen heat-treated portion yielded a somewhat improved density of 8.9 g/cm^3.

To shed further light on the mechanism of oxide reactivation, the as-received oxide and the material resulting from each processing step on each batch were analyzed for fluorine. Table I-1 summarizes the analytical results and the corresponding pellet densities obtained.

It is clear that the oxidation-reduction cycling treatment has removed substantial amounts of fluorine, as well as improved the low temperature sinterability. Heating the fluoridated oxide at the same temperature in nitrogen neither removed such large quantities of fluorine nor restored sinterability. It also appears that the bulk of the fluorine is extracted in the air oxidation step of the oxidation-reduction cycle.

b. Sintering Mechanism

In order to densify a binary material such as uranium oxide, it is clearly necessary to effect the transport of both the anions and the cations, and it appears most probable that in uranium oxide both species move by diffusion. Experiments on the diffusion coefficients of both uranium and oxygen in stoichiometric uranium oxide have shown that the oxygen diffuses much more readily than the uranium ions.[1] For this reason, it has been hypothesized, most reasonably, by J. Williams[2] and co-workers that the rate-limiting process in the sintering of UO_2 is the diffusion of the uranium ions. To account for the enhanced low temperature sinterability of non-stoichiometric oxide, as compared with stoichiometric oxide, it is postulated that the diffusion of uranium ions should be more rapid in the latter. The presence of excess oxygen is connected, therefore, with the increased diffusion rate of uranium ions.

It has been hypothesized further that the enhanced mobility of the uranium ions is due to a decrease in the cationic radius accompanying the increase in positive charge caused by the introduction of excess oxygen. Thus, hydrogen, for example, inhibits sintering by removing excess oxygen and reducing the oxide to stoichiometric composition. This causes the mean uranium ionic charge to be lowered to +4, which increases the ionic size and decreases ionic mobility. In this

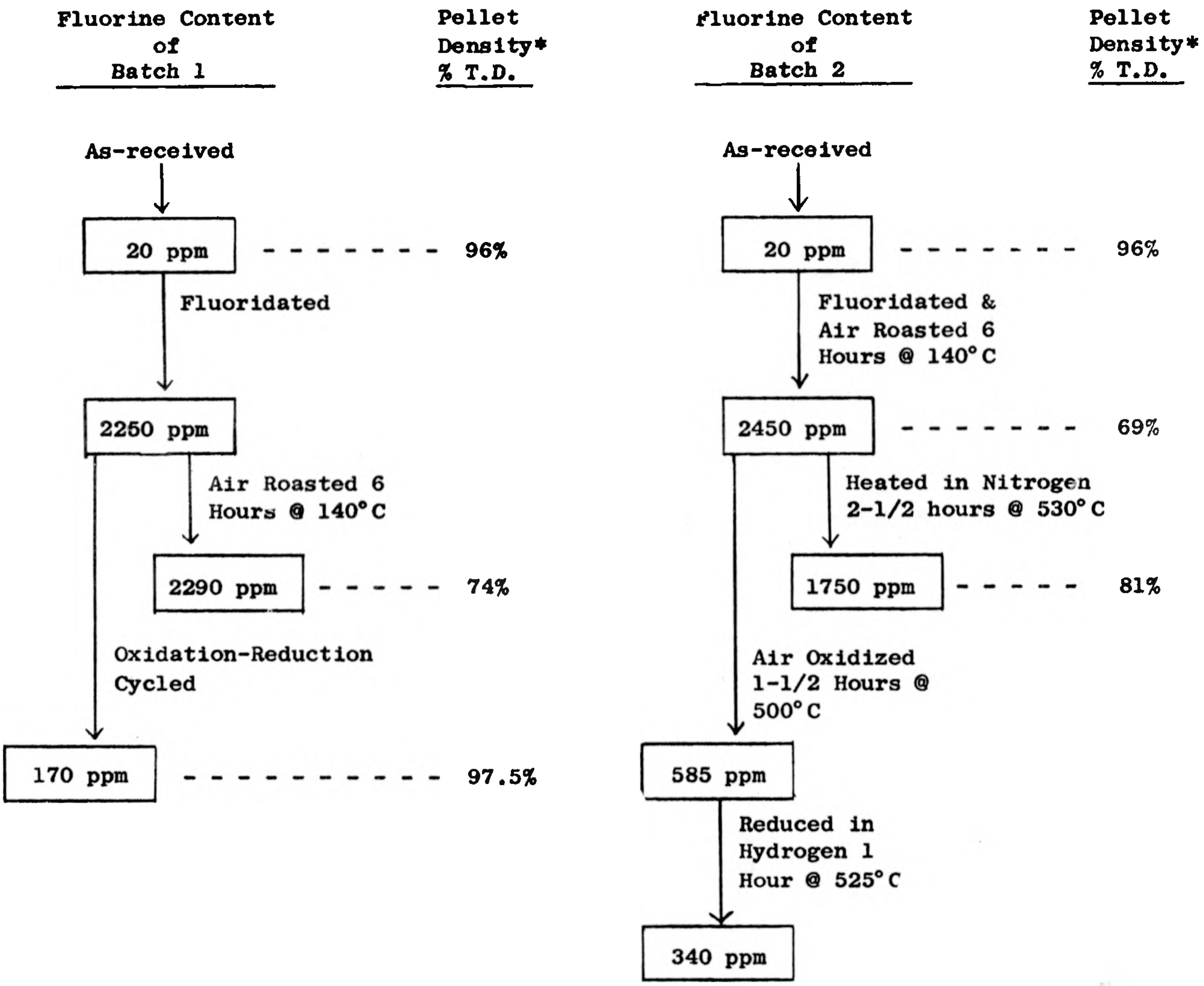
---

[1] J. Belle, "Properties of Uranium Dioxide," Proceedings of Second United Nations Conference on Peaceful Uses of Atomic Energy, Geneva, 1958, P/2404, Vol. 6, p. 580, United Nations, Geneva (1958).

[2] J. Williams, E. Barnes, R. Scott and A. Hall, "Sintering of Uranium Oxides of Composition UO_2 to U_3O_8 in Various Atmospheres," AERE M/R 2653, August 1958.

TABLE I-1

SUMMARY OF DATA RELATING PROCESSING WITH FLUORINE CONTENT AND SINTERABILITY OF DAVISON LOT 0



*After standard sintering at 1300° C for 2 hours in nitrogen followed by 1 hour in hydrogen.

qualitative argument, of course, it is not important whether, in non-stoichiometric oxide, there are two distinct kinds of cations (one having a charge of +4 and the other a charge of +6) or a single species of hybridized cations of intermediate charge.

The inhibition of sintering produced by the presence of fluoride impurity is believed to be somewhat different from that due to hydrogen. The fluoride ion is presumed to occupy a lattice position replacing oxygen and thus tends to decrease the mean positive charge of the uranium ion. The cation mobility and sinterability are correspondingly reduced.

This suggests that other impurities capable of occupying a lattice position will exert a similar influence on uranium ion mobility and, hence, on the sinterability of non-stoichiometric UO_2. Those which increase the mean positive charge of the uranium cations will enhance sinterability, whereas those which decrease the mean positive charge will inhibit sinterability.

Uranium ion diffusion coefficient measurements on non-stoichiometric UO_2 as a function of O/U ratio and of impurity content would demonstrate whether the proposed mechanism is correct. Although the diffusion coefficient of the oxygen ions in non-stoichiometric uranium oxide has been studied,[3] similar measurements on the diffusion of uranium, which is of greater theoretical significance, apparently have not been made.

2. Preparation of Very High Density UO_2

a. Preliminary Experiments

Early in the reporting period, an investigation was initiated aimed at preparing very high density UO_2 pellets by the two-stage nitrogen sintering process. This development effort was prompted by the fact that densities as high as 98% T.D. (10.74 g/cm^3) have sometimes been achieved in past work and that significant advantages might result from the use of such high density fuel in a reactor core. Current fuel specifications call for densities ranging from 93% to 95% T.D. It has already been demonstrated on a laboratory scale that the low temperature process can routinely produce densities in the 95% to 97% T.D. range. To attain densities in excess of 98% T.D., several scoping experiments were conducted to determine which process variable shows the greatest influence in effecting density increases above the 95% to 97% T.D. range.

The initial experiments were performed with oxides which had previously been subjected to one oxidation-reduction cycle and had densified to the 95% to 97% T.D. range under the normal processing conditions, i.e., addition of 0.4% PVA as binder, forming pressure - 19 tsi, sintering temperature-1200°C to 1300°C, and soaking time - two hours in N_2, one hour in H_2.

---

[3] J. Belle and A. B. Auskern, "Oxygen Ion Self-Diffusion in Uranium Dioxide," in "Kinetics of High-Temperature Processes," W.D. Kingery (Ed.), John Wiley & Sons, Inc., New York, p. 44 (1959).

Variations in the compacting procedure were investigated, including the use of a slugging (repressing) technique, elimination of binder and/or lubricant, an increase of forming pressure, and the utilization of a new die designed to produce 1/4-inch diameter pellets. In addition, sintering temperatures up to 1400°C were employed, and the rate of approach to the sintering temperature was varied.

None of these changes in processing, either independently or in combination, led to a significant increase in pellet density.

b. Oxidation-Reduction Cycling Variations

The next phase of this work was concerned with the effects of variations of the oxidation-reduction cycling technique. The variation first investigated involved multiple oxidation-reduction cycling. Compacts from three Davison Lot 3 oxide batches, which had been subjected to single, double, and triple standard oxidation-reduction cycles, respectively, were pressed at 19 tsi and sintered at 1300°C for one hour in nitrogen followed by one hour in hydrogen. The following table summarizes the experimental data obtained:

No. of Ox.-Red. Cycles (a)	Initial O/U Ratio	Bulk Density (After Granulation) g/cm^3	Green Density g/cm^3	Pellet Density(b) g/cm^3
1	2.35	2.33	5.92	10.63
2	2.37	2.10	5.83	10.73
3	2.38	1.88	5.69	10.75

(a) Air oxidation for 1.5 hours at 500°C, followed by reduction in hydrogen for 1 hour at 525°C

(b) Archimedean

All the sintered pellets exhibited good dimensional and physical integrity. The effect of additional oxidation-reduction cycling is shown in (1) the higher initial O/U ratios obtained under the same roasting conditions, (2) the decrease in bulk density, and (3) the increase in pellet density, a maximum of 98.1% T.D.

In view of this pellet density improvement, a 100-gram batch of this oxide was subjected to seven such cycles. The powder bulk density of the resulting UO_2 was found to be 0.71 g/cm^3, which is approximately one-half of the value obtained after a single cycle, The activated oxide was uniformly air-roasted for 16 hours at 160°C to produce an O/U ratio of 2.38. The usual manual granulation procedure yielded unusually small agglomerates which compacted poorly. To form compacts free of laminar cracks, it was necessary to repress (slug) the material as part of the pressing operation. It was possible to produce satisfactory compacts with a forming pressure of

25 tsi after prepressing at 10 tsi. Although the internal lubricant (zinc stearate) concentration was increased from 0.1 w/o to 0.3 w/o, attempts to produce crack-free compacts above 25 tsi were unsuccessful. After sintering at 1300°C, all pellets, including those satisfactorily compacted at 25 tsi, exhibited circumferential cracks and were distorted. The highest density attained was 96.4% T.D. which is approximately 0.5% less than that obtained with Davison Lot 3 treated with one oxidation-reduction cycle.

Because it was believed that the poor forming characteristics of the 7-cycled material had obscured any beneficial effect which may have resulted from the activation treatment, compacting was attempted with machine-granulated, instead of hand-granulated, material. Granulation was performed in a Colton Granulator Model No. 542, and satisfactory agglomerates were obtained after one pass through the 14-mesh screen of the unit. The machine-granulated oxide was compacted without difficulty and sintered at 1300°C in nitrogen for one hour followed by hydrogen for one hour. A maximum density of 10.57 g/cm^3 (96.4% T.D.) was again obtained, this time when a forming pressure of 30 tsi was employed. In contrast with the earlier results, the pellets were free of defects and were dimensionally uniform. Since a density of 98.1% T.D. has already been attained with Davison Lot 3 activated by only three oxidation-reduction cycles, it would appear that there is an optimum number of cycles to achieve maximum density with this starting material.

In another variation of oxidation-reduction cycling, a batch of Davison Lot 3 was oxidized at 500°C for 16 hours, instead of the usual 1.5 hours, and then reduced in hydrogen at 525°C for one hour. The activated material was processed by the standard procedure and compacts were pressed at two forming pressures. After sintering at 1300°C, pellet densities of 98.1% T.D. and 97.8% T.D. were obtained with forming pressures of 20 tsi and 30 tsi, respectively. These densities are essentially the same as those obtained with Davison Lot 3 subjected to three oxidation-reduction cycles. It seems, therefore, that prolonged oxidation may play a role in enhancing sinterability. In this connection, it is worth noting that the oxidation step of the cycle has already been shown to remove fluorine which was acting as a sintering inhibitor.

The reduction temperature of the activation treatment was changed in another experiment to establish its effect on sinterability. A batch of Davison Lot 3 was oxidized at 500°C for one hour and then reduced at 425°C, i.e., 100°C lower than the normal temperature for reduction. The oxidized material was not completely reduced as indicated by the final O/U ratio of 2.31. This oxide was then processed directly into pellets and a density of 96.0% T.D. was obtained after sintering at 1300°C. Although the density fell short of the goal of 98% T.D., the results suggest that air roasting may be eliminated as a pretreatment when the oxide has been activated by oxidation-reduction cycling. This may be accomplished by simply selecting the proper time-temperature schedule for partial reduction in the second step of the treatment. This experiment also demonstrates that complete reduction is not necessary to achieve sinterability enhancement and supports the conclusion that the critical step in the activation procedure is probably the oxidation.

C. Irradiation Testing Program

1. Preparation of Enriched UO_2 Pellets

a. Enriched Oxide Characterization

Enriched oxide (MCW Lot 5, 4.95% U-235) for the irradiation testing experiments was procured from the Mallinckrodt Nuclear Corporation. This material was immediately available from stock and had the additional advantage of being representative of production scale ceramic grade UO_2, having been taken from a 400-pound lot (MCW designation-Lot J 36 GZ). It was learned, however, that the oxide was classified by the supplier as a so-called "dense" type. Since ceramic grade oxide of similar properties had not yet been handled in the process development program, a small quantity of "dense" depleted UO_2 (MCW Lot 4) was obtained at the same time to serve as a pilot material for processing.

The major difference between these two lots and previous oxides received from Mallinckrodt, for example Lot 3, can be seen in a comparison of the bulk densities and wet sieve analyses for the as-received materials shown in Table I-2. Not only does the "dense" oxide have a much higher bulk density, but it is also much coarser than Lot 3.

Additional data presented in Table I-2 also affords a comparison of the depleted Lot 4 with enriched Lot 5. Although the bulk densities, O/U ratios and sieve analyses of the as-received oxides are quite similar, the enriched material appears to be more active on the basis of the higher O/U ratio obtained after air roasting under the same conditions. The bulk densities, after activation by different versions of the oxidation-reduction cycling, are also included.

b. Initial Sinterability Tests

Preliminary sintering experiments at 1300°C were conducted with each lot both with and without activation by oxidation-reduction cycling. In every case, the oxide was air roasted to produce an initial O/U ratio in the range 2.37 to 2.39. Compacts were prepared by the normal procedure involving granulation with 0.4% PVA and blending with lubricant. The forming pressure, however, was varied to determine its effect on pellet density and diameter. These were to be compared with the capsule design density and diameter of 95% T.D. and 0.250 inch, respectively. The pertinent sintering data are summarized in Table I-3.

All pellets exhibited good dimensional integrity with less than a 0.001 inch diametral variation from top to bottom. The surface of the pellets derived from the as-received material was rough, whereas that from the activated oxide was smooth. It is apparent from the data presented that, in the as-received condition, both oxides exhibit relatively poor low temperature sinterability in nitrogen.

TABLE I-2

PHYSICAL PROPERTIES OF MALLINCKRODT OXIDES

Designation	"Standard"	"Dense"	
Lot No.	Lot 3	Lot 4	Lot 5 (Enriched)
O/U Ratio, as received	2.06	2.04	2.07
After air roasting 16 hr. @ 160°C		2.265	2.365
Wet Sieve Analysis, % As received			
+20	-	1.3	2.4
20/40	-	15.2	8.7
40/60	-	22.0	13.9
60/100	-	21.0	19.2
100/200	-	18.1	21.5
-200	99.7	22.4	34.3
Bulk Density, g/cm^3			
As received	1.21	3.05	3.11
After 1 standard ox.-red. cycle		-	2.21
After 1 ox.-red. cycle (16 hr. in air, 1 hr. in H_2)		1.97	2.16
After 2 standard ox.-red. cycles		1.48	-
After 3 standard ox.-red. cycles		1.17	1.41
After hammer-milling		2.33	-
After hammer-milling and 1 standard ox.-red. cycle		1.59	-

TABLE I-3

SUMMARY OF PRELIMINARY SINTERING DATA

Sintering Conditions: 1 hour in N_2, 1 hour in H_2 at 1300°C

		MCW Lot 4 (Depleted)				MCW Lot 5 (Enriched)			
Activation Treatment	Forming Pressure tsi	Green Density g/cm^3	Diametral Shrinkage, %	Sintered Geo. Den. g/cm^3	Final* Dia. in.	Green Density g/cm^3	Diametral Shrinkage, %	Sintered Geo. Den. g/cm^3	Final Dia. in.
As-received	20	6.15	11.1	8.46	-	-	-	-	-
	25	-	-	-	-	6.01	15.2	9.50	0.260
	30	6.41	11.1	8.80	-	6.11	15.1	9.60	0.261
Ox.-Red., 1 Cycle	20	5.76	19.1	10.25	-	5.57	20.3	10.45	0.245
	25	5.97	18.4	10.33	-	-	-	-	-
	30	-	-	-	-	5.95	19.0	10.60	0.249
	35	-	-	-	-	6.11	18.2	10.62	0.252
Ox.-Red., 1 Cycle (Oxid. 16 hr.) (Pressed in 1/2" die)	20	5.64	19.5	10.24	-				
	25	5.95	18.6	10.43	-				
	30	6.11	18.1	10.48	-				
Ox.-Red., 1 Cycle (Oxid. 16 hr.) (Pressed in 0.303" die)	20	5.55	20.0	10.30	0.246	-	-	-	-
	25	5.91	19.0	10.45	0.250	-	-	-	-
	30	6.05	18.9	10.50	0.250	5.99	18.72	10.59	0.250
	35	-	-	-	-	6.12	18.35	10.69	0.251
	40	-	-	-	-	6.28	17.80	10.71	0.254
Hammer-Milled and Ox.-Red., 1 Cycle	30	6.18	17.8	10.48	0.252				
Ox.-Red., 2 Cycles	30	5.99	19.0	10.69	0.249				
Ox.-Red., 3 Cycles	30	5.96	19.4	10.67	0.248				

* Only final diameters of 1/4-inch pellets shown.

While both materials respond satisfactorily to activation by the standard oxidation-reduction technique, the oxidized-reduced enriched oxide appears to be somewhat more sinterable than the similarly treated depleted oxide. Moreover, oxidation for 16 hours, instead of the usual 1.5 hours, leads to densities approaching 98% T.D. for the enriched oxide when forming pressures of 35 to 40 tsi are employed.

It is also noteworthy that multiple oxidation-reduction cycling has markedly improved the sinterability of the depleted oxide, and this result suggests application of a similar treatment to the enriched oxide to maximize density.

c. UO_2 Pellets for Revised Testing Objectives

In view of the results of the above preliminary experiments, it became clear that the high sinterability of the activated enriched oxide would permit broadening of the irradiation testing objectives. The original objectives called for determining the dimensional stability and fission gas retentivity of pellets sintered at 1200°C to 1300°C by the low temperature process. The pellet densities were to be comparable to those being produced by hydrogen sintering to meet existing commercial fuel specifications, i.e., approximately 95% T.D. It now appears, in addition, that (1) the effect of a significant pellet density increase above 95% T.D. could be determined, and (2) the radiation behavior of 95% T.D. pellets sintered at temperatures substantially lower than 1200°C to 1300°C could also be investigated.

Sintering experiments at temperatures lower than 1300°C were then conducted with enriched oxide to establish the processing conditions for attaining maximum density and to find the minimum sintering temperature to accomplish the latter objective. A maximum pellet density of 97.5% to 97.6% T.D. was obtained under different sets of conditions as shown in Table I-4.

TABLE I-4

ENRICHED OXIDE PROCESSING CONDITIONS RESULTING IN MAXIMUM DENSITY[a]

Activation Treatment	Forming Pressure tsi	Sintering Temp.,[c] °C
1 Standard[b] Ox.-Red. Cycle	35	1200 & 1100
	40	1200 & 1100
3 Standard Ox.-Red. Cycles	30	1200
1 Ox.-Red. Cycle (16 hr. oxidation)	35	1200
	40	1200

---

[a] Geometric Pellet Density - 97.5% to 97.6% T.D.
[b] Standard Cycle - 1.5 hr. in air @ 500°C, 1 hr. in H_2 @ 525°C
[c] Sintering Schedule - 1 hr. in N_2, followed by 1 hr. in H_2

The high density reached with the enriched oxide activated by one standard oxidation-reduction cycle and sintered at 1100°C suggested an experiment at an even lower temperature. After sintering at 1000°C for one hour in nitrogen, followed by four hours in hydrogen to remove excess oxygen, the same material densified to 94.5% T.D. A final O/U ratio determination indicated that complete reversion to stoichiometric composition had occurred. It appears, therefore, that satisfactory enriched pellets can be prepared at temperatures as low as 1000°C for irradiation testing.

d. Design Density UO_2 Pellets

The enhanced sinterability of the activated oxide led to a minor unexpected problem involving the preparation of 95% T.D. pellets at 1300°C. These were required as a standard with which the higher density pellets and the 1000°C sintered pellets could be compared. One of the preliminary experiments with the enriched oxide activated by one standard oxidation-reduction cycle (see Table I-3) had already shown that a comparatively low forming pressure would achieve this result; however, the inside diameter of the compacting die would have to be increased to produce the desired sintered pellet diameter, 0.250 - 0.255 inch.

A new die was procured for this work and a sintering experiment was conducted to determine the exact conditions for preparing pellets having the design properties. Enriched oxide activated by one standard oxidation-reduction cycle was compacted at several forming pressures and sintered at 1300°C for one hour in nitrogen followed by one hour in hydrogen. The following table presents the pellet densities and diameters found as a function of forming pressure:

Forming Pressure tsi	Green Density g/cm^3	Diametral Shrinkage %	Final Dia., in.	Geo. Pellet Density, g/cm^3
10	5.06	22.12	0.250	10.20
15	5.35	21.32	0.253	10.41
20	5.59	20.36	0.256	10.53
25	5.80	19.55	0.258	10.61

Under these particular sintering conditions, it is clear that the desired pellet properties can be obtained with a forming pressure of 15 tsi.

In addition to the above experiments with enriched MCW Lot 5, several sintering runs were performed with activated depleted MCW Lot 4 at 1300°C to prepare 95% T.D. UO_2 pellets for capsule mockups.

2. Irradiation Capsule Design

To obtain approval of the capsule design from the Westinghouse Testing Reactor Safeguards Committee, a Hazards Evaluation Report, based on the irradiation of 1/4-inch diameter 4.95% enriched UO_2 pellets in 0.525-inch O.D. uninstrumented capsules, was submitted early in the quarter. Although the design had been tentatively approved earlier by WTR engineers, it was now unacceptable because of a single encapsulation of the NaK thermal bond. This is now prohibited by the latest regulations requiring a double encapsulation of such reactive material.

A revised capsule design following the WTR recommendations was then submitted and was approved.

The detailed capsule design is shown in Figure I-1. The encapsulating material of construction is Type 304 stainless steel. Within an outer capsule is an inner capsule in which two specimen tubes are stacked. The outer capsule length and diameter are 5.5 inches and 0.525 inch, respectively. Each specimen tube is 2 inches long and has a wall thickness of 0.010 inch. Approximately four UO_2 pellets are sealed in each tube. The annular space between the specimen tube and inner capsule is filled with NaK.

Plans call for the irradiation of one capsule to a burnup of 10,000 MWD/T of uranium and two capsules to a burnup of 20,000 MWD/T of uranium. With an assumed effective thermal neutron flux of 7.8×10^{13} neutrons/cm^2-sec., the irradiation period for the former is 5 WTR cycles and that for the latter is 11 WTR cycles. The irradiation conditions selected lead to an average value of 29 watts/cm for the fuel rating,

$$\int_{\text{fuel surface}}^{\text{center}} k\,(\theta)\; d\,\theta$$

(where $k\,(\theta)$ is the thermal conductivity of UO_2 at temperature θ) and an average fuel surface temperature of approximately 400°C. Runnalls[4], in summarizing Canadian work on the radiation behavior of sintered ceramic grade UO_2, notes that a fuel rating of 29 ± 3 watts/cm with a fuel surface temperature of 400°C corresponds to the point where grain growth is discernible. Furthermore, where grain growth has been observed, a substantial quantity of fission gas has invariably been released. In view of the fact that fission gas retentivity is one of the properties to be investigated in this program, it is apparent that a more severe irradiation test would not be desirable.

3. Capsule Fabrication

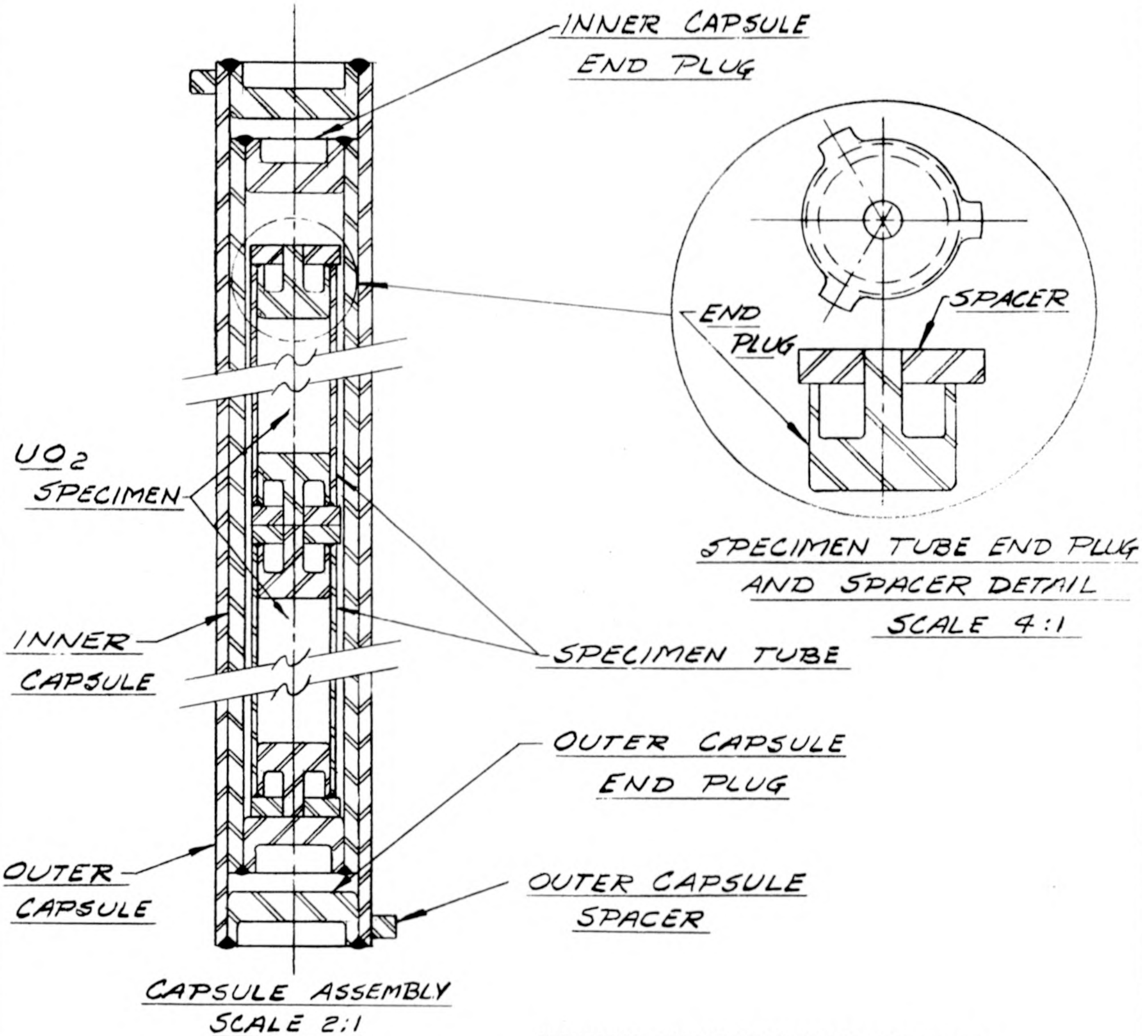
Upon acceptance of the capsule design by WTR, work was initiated on the fabrication of capsule components. An end plug welding fixture was assembled and installed in a helium atmosphere welding dry box. Leak detection and radiographic procedures were prepared for weld inspection.

D. Conclusions

The study of the effect of fluoride additions on the low temperature sinterability of UO_2 in nitrogen emphasizes the need for more fundamental information concerning the sintering mechanism operating in non-stoichiometric oxide. In particular, basic data on the influence of impurities on uranium ion diffusion would be desirable.

---

[4] O. J. C. Runnalls, "Uranium Dioxide Fuel Elements," CRL-55, January 28, 1959.



SPECIMEN TUBE END PLUG AND SPACER DETAIL
SCALE 4:1

CAPSULE ASSEMBLY
SCALE 2:1

PRINCIPAL DESIGN DIMENSIONS AND NOTES

UO_2 Specimens (4 per tube)
Diameter - 0.250 in
Length - 1/4 to 1/2 in
Diametral Pellet Clearance - 0.005 in
Axial Pellet Clearance - 0.125 in

Specimen Tube (304 ss)
ID - 0.255 in
OD - 0.275 in
Length - 2.1 in (max.)

Inner Capsule (304 ss)
ID - 0.344 in
OD - 0.453 in
Length - 5-1/16 in

Outer Capsule (304 ss)
ID - 0.453 in
OD - 0.525 in
Length - 5.5 in

NOTES:
(1) Entire capsule is assembled in helium atmosphere.
(2) NaK (22% Na) is located in annular space between specimen tube and inner capsule.

FIG. I-1 UO_2 IRRADIATION CAPSULE DESIGN

The work aimed at producing very high density UO_2 demonstrates that pellet densities in excess of 98% T.D. are difficult to consistently attain within the limitations of the current processing techniques.

E. Work Plan for the Next Quarter

The preparation and encapsulation of enriched UO_2 pellets for irradiation will be completed. Pre-irradiation testing, such as final O/U ratio determination and metallographic examination, will be performed on representative pellets from each set to be irradiated. The assembled capsules will be inserted in the WTR within the next reporting period.

II. THE DEVELOPMENT OF URANIUM CARBIDES AS A NUCLEAR FUEL FOR LOWERING THE COST OF NUCLEAR POWER (TASK II)

H. S. Kalish, F. B. Litton, J. Crane, M. L. Kohn

A. Introduction

It was shown in the last Quarterly Progress Report (Report No. NYO-2691, dated February 10, 1961) that powdered uranium monocarbide can be produced using either methane or propane as the carburizing medium. Because of the different chemical and thermodynamic properties of propane, extensive work was necessary to determine the parameters required for the production of acceptable powders. The primary attractions for the use of propane are the low residual nitrogen and oxygen concentration, and the high carbon concentration. The work reported previously on propane-produced powders indicated a need for the determination of techniques for elimination of the high free-carbon concentration of these powders. This work was performed during the current report period.

The initial results of a program to determine optimum charge material for arc melting and casting of uranium carbide were reported in NYO-2691, February 10, 1961. The program consisted of preparing five castings from pelletized uranium dioxide and graphite and the same number from uranium carbide prepared by reacting pelletized uranium dioxide and graphite. In the former instance, the carbothermic reduction was carried out in the skull arc furnace. The purpose of research was to provide an indication of compositional control and yield for the two charge materials. In addition, it was expected that particular problems associated with either of the two charge materials would come to light during the preparation of these castings.

A tentative cost estimate was prepared to show comparative costs for castings from the two types of charge materials. The purpose of the estimate was to determine the economic feasibility to guide in the selection of a casting process.

B. Uranium Monocarbide by the Propane Reaction

The experimental work on the preparation of uranium monocarbide by the use of methane as the carburizing gas was completed during the previous report period, and all experimental work during the current period was performed with propane. The objective of this work was to determine the variables affecting the composition of the product from the propane reaction and to study techniques for reducing its free carbon content.

The initial work using the carburizing apparatus described in previous Quarterly Reports, NYO-2689 and NYO-2690, resulted in powders with variable free carbon and very low nitrogen contents. The analyses of all carburizing runs performed during this period are summarized in Table II-1.

1. Carburizing Conditions for the Propane Reaction

The kinetics of the propane reaction were studied as a function of operating variables. Reaction time varied at temperatures from 500°C to 650°C from one-quarter to three hours. Under these conditions with a rate of 2.0 liters per minute propane flow through the retort and a charge of 600 grams uranium metal, the total carbon content of the uranium carbide product varied from 3.6 to 5.8 w/o. The experimental data are shown in Table II-1.

TABLE II-1

SUMMARY OF DATA ON PREPARATION AND ANALYSES OF PROPANE-PRODUCED URANIUM MONOCARBIDE POWDER

Carburizing Conditions		Charge	Retort	Vacuum Diffusion Treatment				Carbon Analyses[(c)], w/o	
Temp., °C	Time, Hrs.	Material[(a)]	Insert	Time, Hrs.	Temp., °C	Vacuum, Microns	Remarks[(b)]	Total	Free
500	1	Derby	None	None	-	-	-	3.6	0.3
500	2	Derby	None	None	-	-	-	3.9	0.2
500	3	Derby	None	None	-	-	-	4.3	0.7
550	1	Derby	None	None	-	-	-	4.4	0.3
550	2	Derby	None	None	-	-	-	4.9	1.0
550	3	Derby	None	None	-	-	-	5.5	1.5
550[(d)]	2	Derby	None	19	650	340	M	5.2	0.15
				1	750	1000			
550	1	Derby	Copper	None	-	-	-	4.1	0.7
550	2	Derby	Copper	None	-	-	-	4.4	1.25
550	2	Derby	Copper	1	750	1000	M	4.2	0.4
550	2	Derby	Copper	1	750	1000	E	4.2	0.5
550	2	Derby	Copper	4	800	210	M	4.5	1.0
550	1	Rod	Copper	None	-	-	-	3.9	0.7
600	0.25	Derby	None	None	-	-	-	4.1	0.5
600	0.50	Derby	None	None	-	-	-	4.7	0.3
600	0.50	Derby	None	None	-	-	-	4.8	1.25
600	1	Derby	None	None	-	-	-	5.2	0.7
650	0.75	Derby	Copper	None	-	-	-	5.8	1.9
650	1	Derby	Copper	None	-	-	-	5.7	0.31
650	1	Rod	Copper	None	-	-	-	5.0	1.4
650	1	Rod	Copper	1	750	1000	E	4.7	0.6

(a) Charge Material: "Derby" - cut sections of small uranium derbies;
"Rod" - lengths of one-inch diameter extruded uranium rod.

(b) M - Diffusion cycle after half of the carburization is completed.
E - Diffusion cycle after completion of the entire carburizing cycle.

(c) Analyses on approximately half of these materials showed less than 100 ppm nitrogen concentration.

(d) This experiment received a double diffusion cycle. The first was performed for 19 hours at 650°C and was followed immediately by a second cycle for one hour at 750°C.

The optimum conditions for forming 4.8 w/o carbon uranium monocarbide were selected at one-half hour carburizing time at 600°C. This product can be obtained, however, by using other carburizing conditions.

The data reported in Table II-1 show that the total carbon content increases with increasing time and temperature, and that the rate of carburization increased with increasing temperature. These data are also plotted in Figure II-1 to show these trends graphically.

Referring to Table II-1, the free carbon content of the specimens does not always follow a consistent pattern. The analyses for both the 500°C and 550°C carburizing sequences indicate general trends for increasing free carbon concentrations with increasing time at temperature. The 600°C sequence did not conform to this observation; of two runs carburized for one-half hour, one had a free carbon concentration of 0.3 w/o and the second 1.25 w/o.

2. Copper Insert in the Carburizing Retort

The carburized product from the propane reaction frequently contained a low density flake material. The deposit occurred on the wall of the Inconel retort and on the stainless steel tiered platform which supported the uranium hydride powder. Analyses indicated that the flakes were predominantly pyrolytic carbon, analyzing about 50 w/o carbon. Handling of the retort causes some of the deposit from the wall of the retort to be mixed with the uranium monocarbide powder produced in this reaction. Samples of the deposit scraped from the walls of the retort indicated the presence of uranium, resulting from some of the uranium powder contacting the walls of the retort during reaction. The propane-produced powder was screened through a -325 mesh screen to remove the flake material.

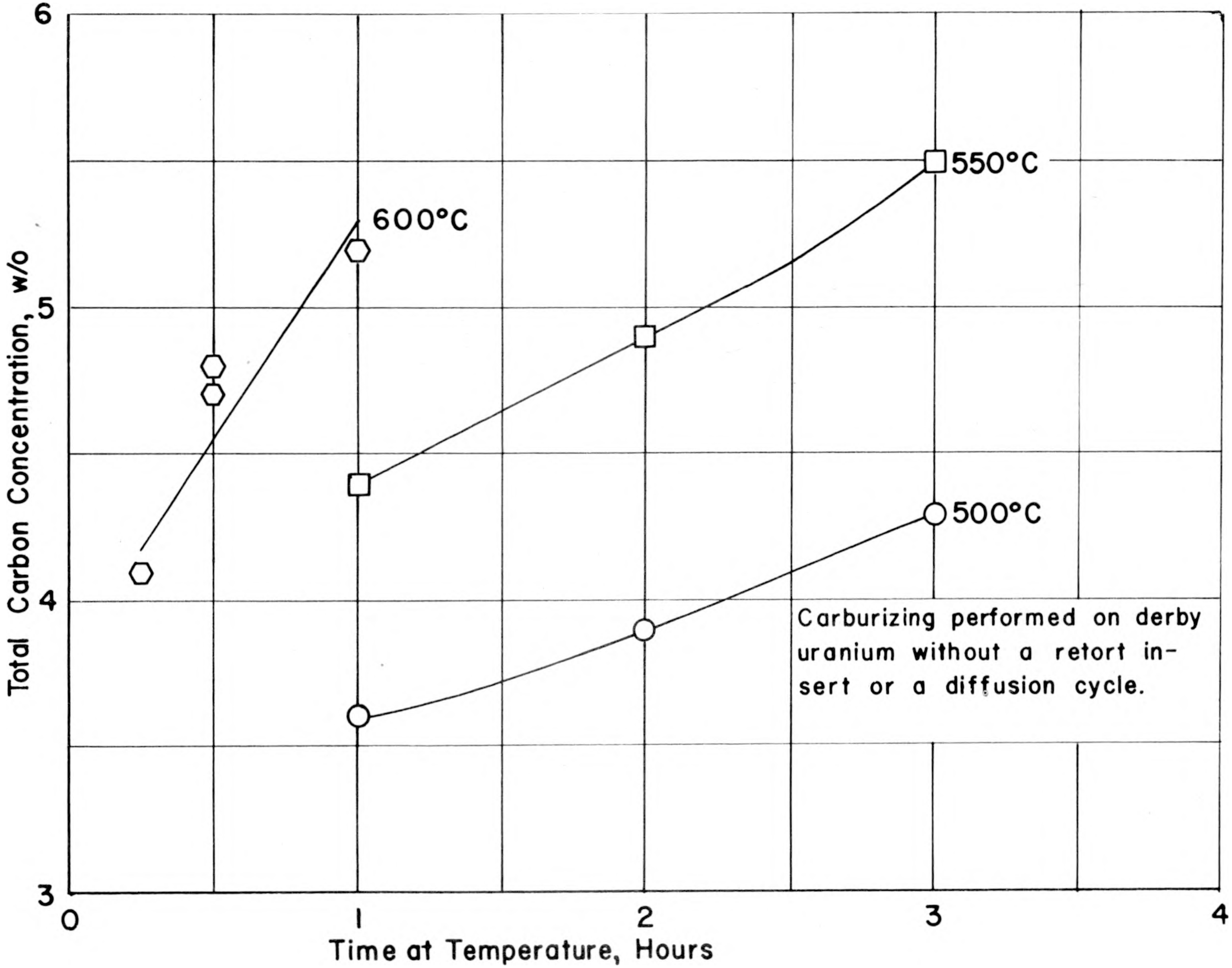
An exploratory test at 550°C carburizing temperature indicated that propane did not decompose as readily on copper as it did on the walls of the Inconel retort or stainless steel tiers. Therefore, a copper insert and a copper tiered support for the uranium were constructed for the retort, Thus, any uranium monocarbide formed would come in contact only with copper. Uranium monocarbide prepared with the copper insert for the retort did not contain flake carbon particles.

The data from four tests in which the copper insert was used with derby uranium charge material are plotted in Figure II-2. The total carbon concentration was reduced 0.3 and 0.5 w/o for the 550°C tests performed for one and two hours, respectively. The use of the copper insert did not affect the free carbon content.

3. Diffusion Cycles

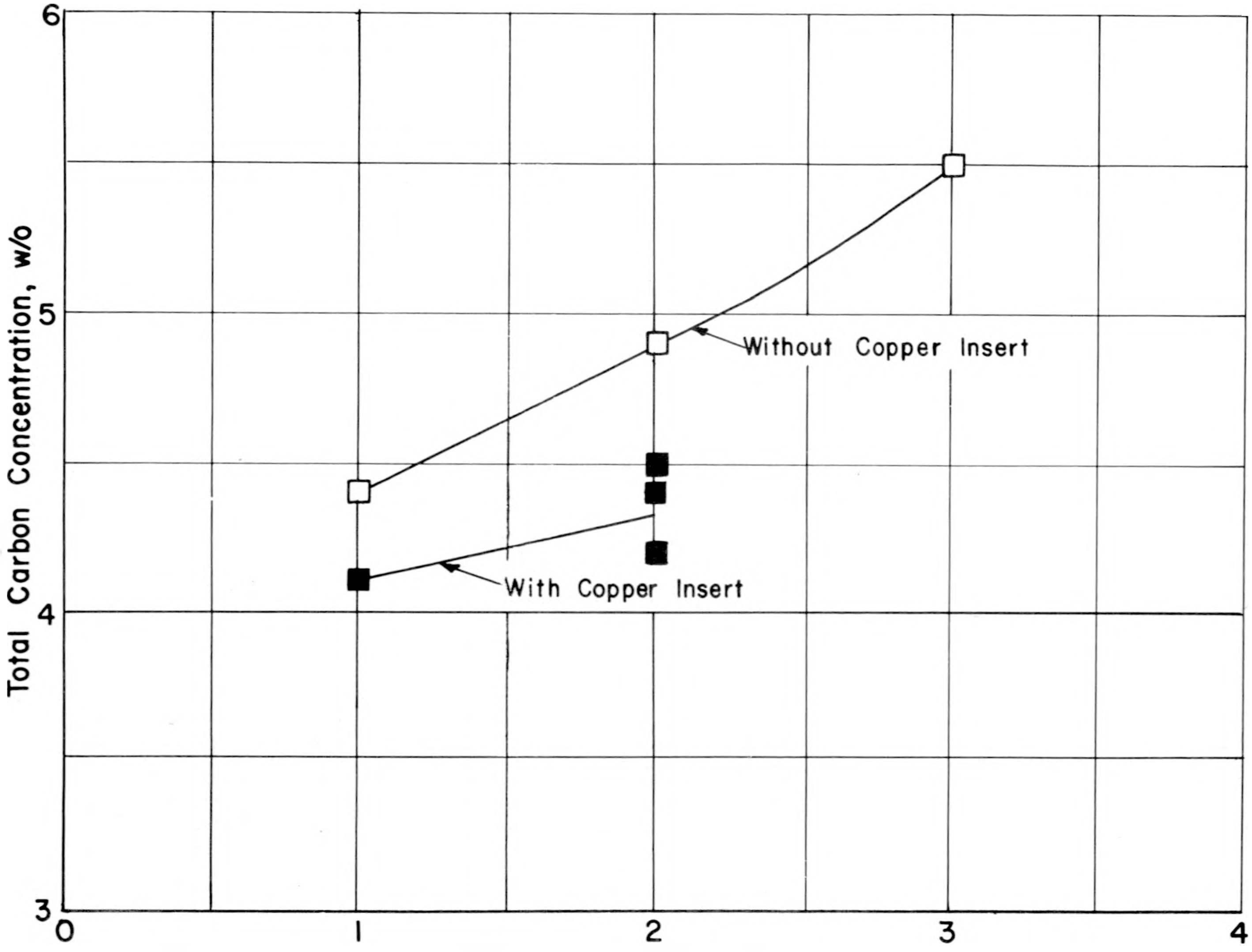
An attempt was made to lower the free carbon content of propane-produced powder by diffusion. The uranium monocarbide powder was heated for various periods at moderately increased temperatures in a propane-free atmosphere. This was done by heating the powder in the retort to either 750°C or 800°C in a vacuum. The diffusion cycle was made, in some tests, after half of a two-hour carburizing cycle was completed and, in other tests, after completion of the total reaction time. In no case was the powder removed from the retort prior to heating. A slight lowering of the free carbon concentration was achieved by this procedure. However, no marked difference in carbon concentration could be ascribed to the diffusion cycle.

Figure II-1



Carburizing performed on derby uranium without a retort insert or a diffusion cycle.

Fig. II-1 Effect of Time and Temperature on Total Carbon Concentration of Propane Produced Uranium Monocarbide.



Time at Temperature, Hours

Fig. II-2 Effect of the Copper Insert on Total Carbon Concentration of Propane Produced Uranium Monocarbide. Charge material was derby uranium. Reaction temperature was 550°C.

Figure II-2

The lack of sensitivity of the powder to a diffusion cycle other than a very long time at moderate temperature can possibly be explained by considering surface absorption of the propane by the carbide. It is well known that propane is readily adsorbed by surface-active materials; thus, if the propane produced uranium acts in this fashion, a short-time, high-temperature diffusion treatment might actually result in an increase in free carbon content by the following mechanism. The adsorbed propane at the higher temperature could break down into free carbon and hydrogen, the latter being pumped off in the vacuum. The free carbon, however, may not have sufficient time to diffuse into the uranium monocarbide. A long-time treatment, on the other hand, at a lower temperature could permit diffusion of the carbon from the adsorbed propane to occur without permitting the decomposition of the propane from taking place. The results from the attempts to use the diffusion cycle for reducing the free carbon content have led to the conclusion that this approach is probably impractical and unnecessary. The long time at a moderate temperature makes the diffusion cycle economically unattractive and since certain runs, such as some of those performed in a half hour at 600°C, lead to free carbon contents of about 0.3 w/o, it was felt that a suitable propane reaction time and temperature could be selected to achieve the right amount of total carbon with sufficiently low free carbon content to permit a satisfactory powder to be produced for subsequent consolidation purposes. The free carbon is uniformly dispersed throughout the powder and, during sintering of the compact produced from that powder, should readily diffuse into the uranium carbide long before the sintering temperature is reached and should have no adverse effect on the sintering characteristics or on the ultimate composition of the consolidated uranium monocarbide.

4. Uranium Charge Material

The uranium monocarbide in the previous sections was prepared from derby uranium. In the process for the production of carbide, the uranium is reacted with hydrogen to form uranium hydride (UH_3) which flakes off the surface of the solid charge material. The carbide product is prepared by heating the thermally unstable uranium hydride in a propane atmosphere in which hydride decomposes into fine uranium particles and hydrogen gas. The uranium particles react with the propane to form the monocarbide. Because of the hot work performed on the rod in the extrusion process, it was though that the hydride particle size produced from the extruded rod might be smaller than that produced from derby uranium. A smaller hydride particle size should, in turn, produce a smaller uranium particle size upon decomposition, thereby causing the reaction with the propane to occur more readily. Thus, it was postulated that the free carbon concentration might be reduced.

Examination of the analytical data shown in Table II-1 indicates that the free carbon concentration of material made from uranium rod was similar to that produced from derby uranium. The uranium charge material had no significant effect on the total or free carbon content of propane-produced uranium carbide powder.

C. Arc Melting and Casting Uranium Carbide

The series of castings using reacted charge material was completed during the previous Quarter; but was re-run because of erratic carbon results in castings made after a change in the skull composition. The initial criteria for comparison of the two charge methods was material losses and casting analyses. The graphite molds were always outgassed prior to melting, and seven of the ten castings reported were made in pre-heated graphite molds.

1. Unreacted Uranium Dioxide-Graphite Charges

A series of five castings made using unreacted charges was completed during this Quarter. The casting procedure was described in the previous Quarterly Report, NYO-2691. Reaction and melting of this type of charge material was carried-out in the skull arc furnace without arc instability. Spatter was substantial during the reaction phase. The extent of spatter is reflected by the high losses and low recovery shown in Table II-2. Values shown in the loss column were obtained by the difference between gross weights before and after melting. The gross weights were adjusted for CO removal. The recovered loss represents that material which was readily picked-up by cleaning the furnace after the casting was made. It does not include material which is not readily recoverable, such as, spatter on heat shields and particles in the dust filter. The average recoverable loss was 56 grams for the five castings, which was less than 30% of the average total loss of 198 grams.

This series of castings was prepared in a skull analyzing 4.9 w/o carbon prior to the first charge. Table II-3 shows a comparison of charge composition with casting analysis. The following observations taken from these data are considered significant:

a. The maximum variation of carbon content from top to bottom of castings was 0.04 w/o.

b. Oxygen content of these castings was below 370 ppm indicating complete reaction of the charge.

c. There was a trend of increasing carbon from the first to the last casting of this series.

The homogeneity of castings made using unreacted charge material appears now to be well established by the data of Table II-3 and that shown in report NYO-2691.

The nature of this melting operation and the size of charge relative to casting imposes the interpretation that the carbon content of the casting is substantially influenced by the skull composition. The trend of increasing carbon content of the castings shows that carbon is picked up during the melting and casting operation. The pick-up of about 0.2 per cent carbon occurs from the graphite electrode during the 18-minute melt and casting period.

The control of carbon content in the casting using a charge of unreacted UO_2-graphite requires adjustment of charge composition to accommodate both increasing carbon content in the skull and carbon "pick-up" in the melt from the electrode. The compensation can be minimized by increasing the charge size relative to the size of the molten pool. For the present equipment this would require continuous feeding of the pellets instead of batch loading.

TABLE II-2

MATERIAL LOSSES DURING REACTION AND CASTING OF URANIUM MONOCARBIDE FROM UNREACTED UO_2-GRAPHITE CHARGES

Casting Identification	Charge Size,* gms.	Casting Weight, gms.	Loss, gms.	Recovered Loss, gms.
11D-25-3SM11	619	780	175	23
11D-26,27-3SM14	724	335	219	56
11D-28,29-3SM17	658	877	75	29
11D-44-3SM21	687	1049	312	75
11D-45-3SM24	745	1415	208	97

---

*UC equivalent of UO_2-graphite plus UC striker.

TABLE II-3

ANALYSES OF CHARGE MATERIAL AND CASTINGS MADE BY SKULL ARC MELTING UNREACTED UO_2-GRAPHITE PELLETS

Casting No.	Charge Composition,(1) w/o C	Casting Composition,(2) w/o			Increase in Carbon Content, w/o C
		Carbon		Oxygen	
		Top	Bottom		
11D-25-3SM11	4.66	5.00	5.01	0.015	0.35
11D-26,27-3SM14	4.64	5.00	4.99	0.037	0.36
11D-28,29-3SM17	4.64	4.95	4.99	0.017	0.33
11D-44-3SM21	4.65	5.26	5.29	0.010	0.62
11D-45-3SM24	4.70	5.46	5.42	0.008	0.75

---

(1) Charge composition was calculated on the assumption that the uranium dioxide is stoichiometric UO_2. An adjustment was made for the carbon content of the striker material.

(2) Nitrogen analyses reported less than 100 ppm.

2. Reacted Uranium Dioxide-Graphite Charges

The results of the series of five castings made from reacted charge material were reported in the last Quarterly Report. Since the casting analyses were erratic due to the use of two different skulls for preparing the series, the new series of five castings was run using one skull under better controlled conditions. The melting and casting procedure for the new series was the same as that used in the previous series.

The charge weights and melting losses are shown in Table II-4. The casting weights are fairly uniform, and the average charge to casting weight ratio is about 0.8. The average loss during melting was 59 grams, ninety-five per cent of which was recoverable. The yield during the carbothermic reduction was greater than 99.5%. This yield is based on the assumption that the reaction proceeded to completion. However, the reaction of the pellets in the induction furnace does not go to completion; total and free carbon contents of the charges, as shown in Table II-5, indicate degree of completion of the reaction.

The change in carbon content from that calculated in the charge to that analyzed in the casting, an average gain of 0.13 w/o, is attributed to "pick-up" from the graphite electrode. The skull analysis at the start of this series was 4.6 w/o carbon and the carbon content of the castings was essentially constant. The maximum variation in carbon content from top to bottom of a casting was 0.09 w/o. The average carbon content for the entire series of five castings showed a spread of only 0.07 w/o. The maximum oxygen content reported for the castings was 420 ppm, indicating essentially complete reaction.

3. Technical and Economic Comparison of Charge Materials for Uranium Carbide Castings

On the basis of castings made to date using both types of charge material the following comparisons can be made:

a. Complete reaction of the UO_2 with carbon is accomplished by either method.

b. Both methods give a cast product low in nitrogen and oxygen.

c. Both reacted and unreacted charges can be melted in the skull arc furnace without arc instability; however, the latter material is demanding of greater technique, and is associated with greater spatter and larger material losses. These losses are about three to four times greater than those occurring with reacted charges.

d. Homogeneity of cast material is good for both forms of charge material, but is slightly better for castings prepared from unreacted charge material.

e. Uniformity of carbon content from casting to casting is better for castings made from reacted charges than from unreacted charges.

TABLE II-4

YIELD OF URANIUM CARBIDE - REACTED CHARGE

Casting No.	Charge Weight, gms.	Theoretical UC in Charge,(1) gms.	Weight after Reacting, gms.	Yield %	Casting Weight, gms.	Melting Loss, gms.	Recovered Loss, gms.
11D-47-S-3SM39	994	812	809	99.6	1043	11	9
11D-48-S-3SM40	1008	824	821	99.6	1106	161	159
13D-1-S-3SM41	998	815	817	100.2	1026	18	17
13D-4-S-3SM42	1010	825	826	100.1	1152	45	40
13D-5-S-3SM43	991	810	806	99.5	1005	62	55

---

(1) Calculation of the quantity of UC which should result from charges, assuming all reactants are fully reacted and no losses occur.

TABLE II-5

ANALYSES OF VACUUM INDUCTION REACTED CHARGE MATERIAL AND CASTINGS MADE BY SKULL ARC MELTING.

The UO_2-Graphite was Mixed and Pelletized to Yield a 1.66 w/o C Theoretical Composition Upon Complete Reaction.

	Reacted Charge Composition, w/o Carbon			Casting Composition,(1) w/o				Increase in Carbon Content,(2) w/o
				Carbon			Oxygen	
Casting No.	Total	Free	Combined	Top	Bottom	Avg.		
11D-47-S-3SM39	5.06	0.30	4.67	4.77	4.72	4.75	0.020	0.09
11D-48-S-3SM40	4.99	0.33	4.66	4.78	4.78	4.78	0.020	0.12
13D-1-S-3SM41	4.83	0.57	4.37	4.86	4.78	4.82	0.026	0.16
13D-4-S-3SM42	4.75	0.10	4.71	4.79	4.85	4.82	0.043	0.16
13D-5-S-3SM43	4.88	0.13	4.73	4.82	4.73	4.78	0.042	0.12

(1) Nitrogen analyses were less than 100 ppm.

(2) Gain in carbon from that calculated in the charge to average casting analysis.

It is clear that further study of the effects of skull composition on the carbon content of the casting is necessary. However, it appears at present that the interaction of charge and skull is of greater significance in the case of unreacted charge material than for reacted charges.

In addition to the technical appraisal, an estimate of comparative casting cost for both types of charge materials was made with a view toward production requirements. The estimate was based on a production rate of 450 Kg. of cast uranium carbide per day, enriched to 3% U-235. A tabulation of the operations, time and materials are shown in Table II-6 and II-7. The major source of recoverable material loss is in the melting operation: 6% from reacted charges, and 35% from unreacted charges. About 600 Kg. of the UO_2-graphite mix is required to produce 450 Kg. of cast UC from reacted charge material; whereas, 855 Kg. of a similar mix is needed to produce 450 Kg. of cast UC from a charge of unreacted UO_2-graphite pellets. Other scrap losses are relatively small compared with those incurred in the melting operation. A summary of the costs is shown in Table II-8.

The results of this cost comparison show that the material losses associated with the use of unreacted charge material outweigh the small advantage in labor and capital equipment cost this method has over the reacted charge material. In addition, the apparently superior control of carbon content from casting to casting in the use of reacted charge material has led to a de-emphasis of further experimental work with unreacted charge material. It is clear that a substantial decrease in material loss must be attained before greater consideration can be given to the use of unreacted charge material. In this connection the further decrease in arc amperage, increase in furnace pressure and, perhaps, a deep crucible to retain spatter losses, are steps which may make the use of unreacted charge material competitive. It is believed significant that these three points can be readily accommodated in an arc reaction and melting operation that might serve as the means for preparation of a consumable electrode.

D. Physical Properties of Uranium Carbide

The major objective of this research is to determine the properties of uranium carbide as a function of compositional and fabricational variables. The work carried out on this project in the past has emphasized methods for preparing uranium carbide of controlled composition and techniques for consolidating the material into useful form. The preparation and consolidation phases of the program have progressed so that meaningful property measurements can be made on material as a function of the variables of interest.

1. Hot Hardness

During this period two attempts were made using a Marshall Hot Hardness Tester capable of operation up to 1600°C at pressures less than 0.1 micron to measure the hot hardness of cast uranium monocarbide (4.8 w/o C) up to 1000°C. The specimens were 3/4 inch diameter x 1/4 inch thick with faces ground parallel. In each instance the

TABLE II-6

OPERATION, TIME AND MATERIAL FOR CASTING FROM UNREACTED UO_2-GRAPHITE CHARGE

Process	Feed Material		Product		Losses - Convertible Material, Kg.*	Labor, man-hrs.	Equipment
	Description	Amount, Kg.	Description	Amount, Kg.			
Weighing	Graphite UO_2	99.18 755.81	UO_2 plus graphite	854.99	8.54	24	Balances, containers, etc.
Blending	UO_2 plus graphite	854.99	Blended UO_2 plus graphite powder	854.99			Containers, rolls, etc.
Compacting	Blended UO_2 plus graphite powder	854.99	UO_2-C pellets	846.45	(6.70)	24	Sixty pellets/min. slow-speed press
Melting and Casting	UO_2-C pellets	846.45	Cast UC	450	241.55 (239.13)	96	Four skull furnaces; 50 Kg. skull capacity each
TOTAL					(245.83)	144	

* Bracketed number is the uranium loss equivalent.

TABLE II-7

OPERATION, TIME AND MATERIAL FOR CASTING FROM REACTED UO_2-GRAPHITE CHARGE

Process	Feed Material		Product		Convertible Material Kg.*	Labor, man-hrs.	Equipment
	Description	Amount, Kg.	Description	Amount, Kg.			
Weighing	UO_2 powder Graphite powder	525 69	-	594.21		24	Balances, containers, etc.
Blending	UO_2-graphite powder	594.21	-	594.21	5.94		Containers, rolls, etc.
Compacting	Blended powder	594.21	UO_2-C pellets	588.27	(4.63)	17	Sixty pellets/min. slow-speed press
Reaction	UO_2-C pellets	588.27	UC pellets	478	3.17 (3.01)	72	Three 150 KW multi-station induction furnaces with accessory vacuum equipment
Melting and Casting	UC pellets	478	Cast UC rods	450	28 (26.6)	48	Two skull furnaces; 50 Kg. skull capacity each
TOTAL					(34.24)	161	

* Bracketed number is the uranium loss equivalent.

TABLE II-8

PRELIMINARY COST ESTIMATE FOR CASTING URANIUM CARBIDE FROM REACTED AND UNREACTED CHARGE MATERIALS

	Estimated Cost per Kg. UC	
	Reacted UO_2-C	Unreacted UO_2-C
Material Cost		
Conversion UF_6 to UO_2	$ 9.50	$ 9.50
UO_2 Use Charge (4%)*	0.97	2.15
Graphite	0.17	0.24
Scrap Reconversion	2.86	20.50
Unrecoverable Material Loss	0.90	1.29
Depreciation of Special Equipment	0.37	0.19
	$14.77	$33.87
Labor (man-hours)	0.36	0.32

*Based on in-process material for 1.5 months; reprocessing material for two months.

uranium carbide sample fractured under a load of five kilograms. The sapphire indenters cleaved at the time of fracture of the uranium carbide.

It is possible that breakage of the sapphire indenters occurred as a result of improper crystal orientation. New indenters were ordered and the location of the basal plane will be determined in reference to the surface of the mounted sapphire indenter prior to hardness measurements.

2. Compatibility Tests

Tests were started to determine the compatibility of uranium carbide with beryllium, Type 304 stainless steel, niobium, tungsten, Zircaloy-2, molybdenum, vanadium, titanium and tantalum.

Cast uranium carbide discs, 1/4 inch thick x 5/8 inch diameter, were clamped in mild steel fixtures between two pieces of the test metal. The test fixtures were heated to 800°C in vacuum for 100 hours. During this test, the specimen temperature varied from 792°C to 802°C. All the materials tested were compatible with cast uranium carbide under these conditions.

3. Thermal Expansion

The thermal expansion of cast uranium carbide containing 4.85 w/o carbon was directly determined on a Leitz Dilatometer. The specimen was ground from cast 7/16 inch rod to 8 millimeters diameter by 25 millimeters long. The thermal expansion was 12.55×10^{-6} in./in./°C.