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HEAVY WATER ORGANIC COOLED REACTOR

THE PREPARATION OF URANIUM CARBIDE FROM ECONOMICAL URANIUM COMPOUNDS

By

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A Joint Venture for Heavy Water Organic Cooled Reactors

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ABSTRACT

The preparation of uranium carbide (UC) from uranium tetrafluoride, ammonium diuranate (ADU) and uranium trioxide (UO_3) has been studied on a gram scale to establish basic process parameters for economic comparison with the conventional UO_2 to UC fabrication method. The process developed in each case involved compacting blended powders (which were, respectively, $\text{UF}_4\text{-SiO}_2\text{-C}$, $(\text{NH}_4)_2\text{U}_2\text{O}_7\text{-SiO}_2\text{-C}$, and $\text{UO}_3\text{-C}$) and heating in vacuum in stages to (1) convert the uranium compound to UO_2 at temperatures up to 850°C and (2) carbothermically reduce the resulting UO_2 to UC at temperatures above 1300°C . The SiO_2 was used in the ADU conversion to remove a fluorine contaminant without uranium loss. Uranium carbide of controlled carbon content and low oxygen content was produced from each of these compounds.

Uranium carbide was prepared from ADU in 20-kg quantities to demonstrate production scale-up of one of the processes studied. The UC produced was of equivalent or better quality than that produced from UO_2 under similar conditions.

An economic comparison indicates that there are potential savings in using each of these materials, depending on the uranium source, instead of UO_2 for UC production. Quantitative evaluation of experimental results and overall economics indicates that only marginal savings may be gained by using ADU and UO_3 ; but a cost reduction is expected using UF_4 .

I. INTRODUCTION

A. GENERAL

Because of its desirable physical properties, UC has considerable promise as a fuel for nuclear power reactors. The Heavy Water Organic Cooled Reactor (HWOCR) is one current reactor program for which UC is the reference fuel. AI, along with other companies, is involved in the development of UC technology. In particular, a process for the fabrication of the HWOCR core is under development at AI. The process consists of (1) synthesizing UC melt stock by the carbothermic reduction of uranium dioxide, (2) casting the melt stock into UC rods by a carbon-arc skull melting and tilt-pour casting method, (3) machining the surface of the UC castings, (4) loading and welding the sintered aluminum product (SAP) fuel tubes, and (5) assembling the clad fuel into elements. Methods of reducing fabrication costs are inherent in this development. The study reported was carried out to investigate the preparation of UC melt stock from UO_2 precursors or other economical uranium compounds as part of this cost reduction effort. The raw materials selected were uranium tetrafluoride (UF_4), ammonium diuranate (ADU), and uranium trioxide (UO_3).

B. URANIUM RAW MATERIALS

Natural uranium is recovered from uranium ores and concentrated as UO_3 powder. Therefore, UO_3 is considered the most economical raw material for preparation of UC, normal in U^{235} content.

The two sources of enriched uranium are the gaseous diffusion plant and the reprocessing plant. The product of the gaseous diffusion plant is UF_6 , which would be the most economical raw material for UC preparation. However, there are no known production methods for direct conversion of UF_6 to UC, although reports have indicated certain methods are technically feasible.⁽¹⁻³⁾ The current practice consists of converting UF_6 to uranium metal or UO_2 and then preparing UC from these raw materials by a variety of methods.⁽⁴⁾ However, UF_4 (an intermediate in the production of uranium metal from UF_6) and ADU (an intermediate in production of UO_2 from UF_6) are considered more economical raw materials.

The uranium product of the (Purex-type) aqueous reprocessing plant, where the uranium was initially spent nuclear fuel or cold scrap, is uranyl nitrate solution. Normally, this material would be converted to UF_6 and recycled back through the gaseous diffusion plant. The uranium can also be converted readily to UO_3 or ADU, raw materials which would be economical for UC preparation.

C. PRIOR WORK

Uranium carbide has been prepared from UF_4 by several methods. Murbach⁽⁵⁾ at AI has applied for a patent on the preparation of UC by reaction of a UF_4 - SiO_2 -C mixture. His work, although limited to a few exploratory tests, served as a basis for the UF_4 studies in this report. A process developed by Sylvania⁽⁶⁾ produced UC from mixtures of UF_4 - Si -C with yields of about 80%. The UF_4 was obtained by reacting gaseous UF_6 with solid silicon.

The thermal decomposition of ADU to U_3O_8 was studied by workers at Battelle.⁽⁷⁾ Uranium carbide has been prepared from ADU by Carborundum^(8, 9) but serious difficulty in product control was indicated. The preparation of UC from U_3O_8 ⁽¹⁰⁾ and UO_3 ⁽¹¹⁾ has also been reported.

II. EXPERIMENTAL

A. MATERIALS

It was decided at the outset that the commercial grade of uranium materials, rather than the high purity research grade, would be studied so that processing methods developed would be readily adaptable for quantity production of UC. The raw materials used in this study were:

UF_4 — depleted uranium derived from UF_6 , -100 mesh powder, 75.6 wt % U, 24.2 wt % F, and 0.2 wt % H_2O

ADU — depleted uranium derived from UF_6 , -100 mesh powder,

Lot 1 — 73.5 wt % U, 2.6 wt % F, 3.2 wt % NH_4 , and 3.3 wt % H_2O

Lot 2 — 77.0 wt % U, 1.8 wt % F, 4.5 wt % NH_4 , and 0.5 wt % H_2O

UO_3 — depleted uranium, normal fluid bed product, -100 mesh powder, and 82 wt % U

C — nuclear grade graphite, -200 mesh powder

SiO_2 — diatomaceous silica products, Celite-analytical filter aid

Si — purified metal, -325 mesh

B. EQUIPMENT

To carry out the variety of tests required in this study, three vacuum furnace systems were used. A resistance furnace with chromel-alumel thermocouple temperature control was employed for tests below 1000°C . Since reaction gases are toxic, the vacuum system exhaust was connected to a filtered laboratory exhaust. The furnace chamber held up to five, 1-in. sample containers. Outgassed ATJ graphite crucibles were used as sample containers with all furnace systems.

The other furnace systems were high temperature (suitable for tests in excess of 2000°C) induction furnaces. The furnace used for the gram scale experiments consisted of a cylindrical quartz reaction chamber, 3-1/2-in. OD, connected to a vacuum system capable of evacuating the furnace to 10^{-5} torr. Heating power was supplied by a 5 kw high frequency induction generator. The quartz chamber contained a graphite crucible, 2-1/4 in. OD, which accommodated

up to four smaller sample crucibles. With this assembly, four individual samples could be reacted simultaneously under identical conditions to evaluate the effect of different compositions. The larger crucible was held stationary in the chamber by several layers of graphite felt insulation and had a removable graphite cover also insulated to reduce thermal radiation losses. This crucible served as the susceptor for the induction generator and provided a reasonably constant temperature reaction zone. Temperatures were measured with an optical pyrometer sighted into the hot zone through a window and a prism located above a centrally located channel in the crucible cover.

The kilogram-scale experiments were carried out in a commercial (42-in. diameter) cold wall, vacuum induction furnace. A cylindrical graphite tube served as the susceptor for the internally located, water-cooled copper, induction coil. The graphite crucible and charge were positioned within the susceptor tube. Thermal insulation was provided radially and on the bottom by layers of graphite felt. An insulated graphite lid was also used to reduce heat losses and prevent particles from being swept out of the charge by rapid reaction. Temperatures were measured by an optical pyrometer sighted on the charge through a window in the furnace wall and a channel in the crucible lid. A mechanical pump with a capacity of 300 cfm was used to evacuate the furnace chamber to an ultimate of 10^{-3} torr.

C. PROCEDURE

The procedure followed in these experiments was to first study the conversion of each uranium material to UO_2 and then study the overall reaction to prepare UC.

In all cases, the preparation of UC involves a solid state reaction which requires intimate contact between reactant particles. To accomplish this, weighed reactants were dry-blended for 1 to 2 hours and then consolidated. The mixing requirements for these reactants were no more stringent than needed to mix ceramic grade UO_2 and carbon for UC preparation. For the small-scale experiments (usually 10 to 15 gm per test) consolidation was by dry-pressing into pellets, 1/2 in. in diameter and 1/2 in. long, having densities from 3 to 5 gm/cm³. For the large scale charges, reactants were wet-agglomerated into spherical particles, approximately 1/4 in. diameter, having densities from 2 to 3 gm/cm³.

A polyvinyl alcohol-water solution containing 68 gm PVA per liter of distilled water was used in agglomerating with about 350 ml of solution required per kilogram of powder. To remove moisture, agglomerates were dried prior to reaction.

It was noted that reactants containing Lot 1 ADU tended to cake during dry-blending. However, suitable mixing was achieved by periodically interrupting the mechanical blending and manually stirring the mixture. The tendency toward caking was attributed to the high H_2O content (3.3 wt %) in this ADU and should be eliminated by predrying the powder.

The typical heating cycle employed in the preparation of UC consisted of two consecutive stages: a low temperature stage followed by a high temperature stage. The low temperature stage, which converted the uranium materials to UO_2 , consisted of heating the reactants in about 1/2 hour to $850^\circ C$ and holding for about 1 hour. The high temperature stage, which converted UO_2 to UC, consisted of heating rapidly to $1300^\circ C$, then gradually heating to the final finishing temperature, and holding until reaction was complete, as evidenced by a pressure equivalent to the background of the vacuum system.

The UC products were cooled in vacuum or a partial helium atmosphere, removed from the furnace, weighed, and placed in a glove box containing a purified argon atmosphere for sampling, examination and storage. Samples were analyzed by standard methods: Combustion for carbon, inert gas fusion for oxygen, either colorimetric or spectrographic for silicon, colorimetric for ammonium and fluorine, volumetric for uranium, and polarographic for O:U ratio. The oxygen and carbon values listed in the results are an average of two to five individual determinations.

III. RESULTS

A. UF_4 STUDIES1. Conversion of UF_4 to UO_2

The results of experiments to study the conversion of UF_4 to UO_2 by reacting UF_4 with SiO_2 are given in Table 1. In these experiments, the samples were heated for about 1 hour in vacuum to the indicated temperature and held for 1/2 hour, or until a final pressure of about 10^{-2} torr was attained. The reaction began below 600°C , was very rapid at 700°C , and was essentially finished at 800°C . Only minor reduction in residual fluorine content occurred at higher temperatures. The gaseous SiF_4 was readily removed from the solid product without measurable reaction with carbon, which was added in several of the experiments. The products were reddish brown in color, characteristic of UO_2 .

TABLE 1
CONVERSION OF UF_4 TO UO_2 WITH SiO_2 IN VACUUM

Run No.	Input	Temper- ature (°C)	Weight Loss		Product Composition			
	mole $\frac{\text{SiO}_2}{\text{UF}_4}$ ratio		% of Input	mole $\frac{\text{SiF}_4}{\text{UF}_4}$ ratio	Fluorine		Silicon	
					(ppm)	% (Removed)	(wt %)	% (Removed)
1	0.700	850	22.4	0.768	-	-	-	-
2	0.800	850	24.0	0.834	-	-	-	-
3	0.900	850	25.8	0.920	-	-	-	-
4	0.990	800	27.1	0.977	830	99.71	0.035	99.7
5	1.000	850	27.6	0.988	700	99.75	0.050	99.5
6	1.000	900	27.5	0.983	730	99.74	0.070	99.3
7	1.010	900	27.4	0.990	350	99.87	0.170	98.4
8	1.034	850	27.4	0.990	340	99.88	0.335	96.8
9	1.050	850	27.4	0.991	315	99.89	0.495	95.2
10	1.100	850	27.2	0.994	205	99.93	-	-

- No analysis

The data indicate the product contains about 700 ppm each fluorine and silicon for a SiO_2/UF_4 mole ratio of 1.00. A slightly higher SiO_2/UF_4 ratio is required to accomplish >99.8% removal of fluorine. Since perfect mixing is seldom achieved, this requirement of a slight excess of one reactant for complete reaction of the other reactant is not uncommon for a solid state reaction. With higher SiO_2/UF_4 ratios, the residual silicon content was much higher. However, as explained later, some residual silicon is beneficial in the carbothermic reduction of this UO_2 to UC. Of course, for a process in which UO_2 is the end product, the SiO_2 input would probably be a compromise between that required for complete fluorine removal and that which produces a tolerable residual fluorine and silicon content.

The weight loss for each experiment is plotted as a function of the input blend in Figure 1. Good agreement of the data is evident. The plot verifies

Figure 1. Conversion of UF_4 to UO_2 with SiO_2 in Vacuum at 800 to 900°C

TABLE 2
PREPARATION OF UC FROM UF_4

Run No.	Input		Reaction Time (hr)		Weight Loss (wt %)		Product Composition			
	SiO_2 mole $\frac{SiO_2}{UF_4}$	Carbon mole $\frac{C}{UF_4}$	Total	At Temperature*	Experimental	Theoretical†	Carbon (wt %)	Oxygen (ppm)	Fluorine (ppm)	Silicon (ppm)
1	1.01	2.95	5-1/2	2	39.4	39.4	4.57	1500	-	-
2	1.01	3.00	5-1/2	2	39.5	39.4	4.66	1500	-	<10
3	1.01	3.05	5-1/2	2	39.3	39.4	4.76	450	15	75
4	1.01	3.11	5-1/2	2	39.4	39.4	4.94	270	30	310
5	0.99	2.97	6-1/2	1-1/4	39.2	39.3	4.59	-	-	-
6	0.99	3.00	6-1/2	1-1/4	39.3	39.3	4.67	-	-	105
7	0.99	3.03	6-1/2	1-1/4	39.4	39.4	4.73	1000	-	90
8	0.99	3.02	8	2	39.3	39.3	4.71	1170	-	10
9	0.99	3.05	8	2	39.6	39.4	4.75	820	50	115
10	0.99	3.07	8	2	39.3	39.4	4.82	445	40	110
11	0.99	3.10	8	2	39.7	39.5	4.94	320	-	105

-No analysis

*Maximum temperature of 1750°C

†Based on a pure uranium carbide product with no loss of uranium in the reaction.

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Figure 2. Carbon Content of UC Prepared from UF_4 as a Function of Carbon Input

that the amount of SiO_2 in the blend is optimum at a mole ratio of about 1.00 (the intersection of the solid lines). The decreasing effectiveness of excess SiO_2 is also evident.

Although SiF_4 is a heavy toxic gas (boiling point of -65°C), the small quantities involved in this study did not present a serious problem. However, large scale production of UC from UF_4 would be concerned with the disposition of SiF_4 . SiF_4 readily dissolves in water and could be drained away in dilute solutions, or the corrosive fluorine could be removed by precipitation as calcium fluoride by the addition of calcium oxide,⁽¹²⁾ though it would be more economical to collect and concentrate the gas for direct resale or recovery of fluorine since fluorine compounds are generally valuable. In that case it would probably be better to carry out the fluoride evolution in a specially designed apparatus, although the complete conversion to carbide can be accomplished in one apparatus.

2. Conversion of UF_4 to UC

The results of experiments using the two-step reaction, $\text{UF}_4 + \text{SiO}_2 + 3\text{C} \xrightarrow{<800^\circ\text{C}} \text{UO}_2 + 3\text{C} + \text{SiF}_4 \uparrow \xrightarrow{>1300^\circ\text{C}} \text{UC} + 2\text{CO} \uparrow$, to convert UF_4 to UC are given in Table 2. In general, the data indicate UC can be readily prepared from UF_4 . The as-reacted carbide pellets were metallic gray in color, somewhat porous, and usually contained visible cracks. The geometric density of the carbide pellets averaged 6 to 8 gm/cm³ and the immersion density (in CCl_4 at room temperature) averaged 10 to 12 gm/cm³. However, solid dense pellets would not be expected in view of the large weight loss, $\sim 40\%$, which occurs in the reaction. The close agreement between the actual weight loss and the expected weight loss indicates negligible loss of uranium in this process.

The carbon content of the carbide products is plotted as a function of the carbon input in Figure 2. These data show that any desired carbon content can be consistently obtained in this process. To produce carbide with 4.80 wt % C, a C/ UF_4 mole ratio of about 3.06 is required. The oxygen content of this carbide was consistent with that expected based on the carbon content, i. e., for hypostoichiometric UC the lower the carbon content the higher the oxygen content. The nitrogen content of several of the carbide products was determined to be about 50 ppm. These oxygen and nitrogen contents are similar to those obtained in the carbothermic reduction of ceramic grade UO_2 under the same conditions.

After the high temperature reaction step, the as-reacted carbide contained a residual fluorine content of 15 to 50 ppm and a residual silicon content of about 100 ppm. However, these levels of residual fluorine and silicon did not present a serious problem since arc melting the carbide in a partial argon atmosphere lowered the residual content of both elements to <10 ppm.

The results of experiments to determine the effect of using an excess of SiO_2 in the conversion of UF_4 to UC are given in Table 3. As expected, the residual fluorine content was lower (even though some remained), and the residual silicon content was higher, than obtained with just sufficient SiO_2 for this reaction (~ 1.00 mole SiO_2 per mole UF_4). However, the residual oxygen contents were much lower than expected for the hypostoichiometric UC products. Also, the product carbon contents were slightly lower than obtained for the same carbon input in experiments without excess SiO_2 . This suggests that the excess SiO_2 was carbothermically reduced during the reaction. It is postulated that the silicon phase (metal or alloy) which remained aided oxygen removal in the high temperature step by action similar to that of platinum flux in the vacuum fusion analysis for oxygen in metals.

TABLE 3
PREPARATION OF UC FROM UF_4 WITH EXCESS SiO_2

Run No.*	Input		Weight Loss (wt %)		Product Composition			
	SiO_2 mole ratio	Carbon mole ratio	Experimental	Theoretical†	Carbon (wt %)	Oxygen (ppm)	Silicon (ppm)	Fluorine (ppm)
	$\frac{\text{SiO}_2}{\text{UF}_4}$	$\frac{\text{C}}{\text{UF}_4}$						
A	1.04	3.06	39.6	39.5	4.79	300	10	13
B	1.04	3.00	39.3	39.4	4.62	180	800	15
C	1.04	2.96	39.4	39.3	4.53	210	900	20
D	1.08	3.00	39.6	39.6	4.50	190	1200	6

*Reaction Conditions: 5-1/4 hours total heating time with 2 hours at the maximum temperature of 1750°C

†Assuming a $\text{UC}_{1.0}$ product, no uranium loss and vaporization of all silicon

B. ADU STUDIES

1. Conversion of ADU to UO_2

Since ADU is a complex compound⁽¹³⁾ (it can vary widely in composition — especially in U content and NH_4/U ratio — depending on preparation conditions), the initial experiments were made to characterize the as-received ADU as a means of predicting the course of the subsequent carbide reaction. Results of heating ADU in vacuum are given in Table 4. The results indicate that H_2O is

TABLE 4
THERMAL DECOMPOSITION IN VACUUM OF ADU* TO URANIUM OXIDES

Reaction Temperature† (°C)	Weight Loss	Product Composition				Product Color
		Uranium (wt %)	O:U Ratio	Fluorine (wt %)	NH_4 (wt %)	
Room Temperature	3.3	75.0	-	-	3.3	Orange Yellow
200	7.6	-	-	-	0.48	Dull Yellow
400	9.6	81.3	2.96	2.80	0.21	Yellow Green
575	11.1	-	-	-	-	Light Green
600	11.9	83.1	2.76	1.33	0.019	Olive Green
650	11.8	83.5	2.69	1.53	-	Dark Green
700	12.2	84.0	2.66	0.92	0.004	Dark Green
900	12.9	-	-	-	-	Black

*ADU Lot No. 1 (73.5 wt % U, 3.2 wt % NH_4 , 2.6 wt % F, and 3.3 wt % H_2O)

†Heated in several hours to temperature and held 1 to 3 hours.

-No analysis.

vaporized at room temperature, ammonium is removed below 400°C (with much of the reaction occurring at <200°C), and the resulting oxide (UO_3) decomposes at U_3O_8 at $\leq 650^\circ\text{C}$. Negligible reduction occurred below the U_3O_8 composition. There was very little loss of fluorine (probably present in ADU as UO_2F_2 or NH_4UF_5) up to 400°C but a noticeable loss at and above 600°C. The loss of fluorine probably occurred by formation of a volatile uranium fluoride since a uranium balance indicated some loss of uranium, and a thin greenish film (not

chemically analyzed) collected in cooler areas of the reaction chamber for each test at or above 600°C. The observed product colors were in general agreement with those reported at BMI⁽⁷⁾ for ADU heated in air.

The results of experiments to determine the amount of carbon consumed in the conversion of ADU to UO_2 , and the effect of SiO_2 to remove fluorine without uranium loss, are given in Table 5. The color of the products depended on the temperature, being green at 500 to 575°C, black at 650 to 725°C, and red at $\geq 850^\circ\text{C}$. Results of Run 1 show that all ammonium was removed at 500°C and that removal of ammonium did not consume any carbon. As expected, carbon was consumed at higher temperatures as the oxide was being reduced. The carbon consumed in converting ADU to UO_2 was about 0.5 mole C/mole U.

Samples of gases evolved in vacuum at 300 and 600°C from ADU and from ADU-C mixtures were analyzed by mass spectrometer. The vapors identified as major constituents were N_2 and H_2O ; minor constituents identified were O_2 , CO_2 , NH_3 , and H_2 .

TABLE 5
CONVERSION OF ADU TO UO_2 BY REACTION WITH CARBON IN VACUUM

Run No.	Input*		Reaction Temperature† (°C)	Weight Loss (wt % of Input)	Product						
	Carbon	SiO ₂			Carbon (wt %)	Reacted Carbon mole $\frac{\text{C}}{\text{U}}$ ratio	Uranium		O:U Ratio	Fluorine (wt %)	NH ₄ (ppm)
							(wt %)	Loss§ (% of Input)			
1	11.23	1.70	500	10.2	12.63	0	70.0	0.1	2.87	2.07	20
2	5.20	0	575	11.2	5.35	0.12	-	-	-	-	-
3	5.20	0	650	12.8	4.94	0.25	-	-	-	-	-
4	11.23	1.70	675	13.0	11.97	0.26	73.5	0.1	2.50	0.76	20
5	5.20	0	725	14.6	4.47	0.39	-	-	-	-	-
6	5.20	0	850	16.7	4.21	0.47	83.1	0.7	2.01	0.90	35
7	11.23	1.70	850	17.2	11.74	0.49	77.1	0.2	2.01	0.05	-
8	5.63	0	900	19.1	4.70	0.52	82.9	3.2	2.00	0.30	7

*Remainder, ADU Lot No. 1 (73.5 wt % U, 3.2 wt % NH_4 , 2.6 wt % F, and 3.3 wt % H_2O). Amount of SiO_2 was based on removal of fluorine as SiF_4 .

†Heated to temperature in ~1 hr and held for 1 to 4 hr.

‡Calculated based on uranium input and uranium analyses of the product.

-No analysis

The conversion of ADU to UO_2 by carbon in vacuum is postulated as taking the form (neglecting fluoride impurity in ADU),

The presence of nitrogen as a major vapor constituent suggests that ammonia decomposed or that some interaction of reaction gases occurred. However, a different mechanism for the reaction cannot be ruled out.

The uranium balance indicates a loss of uranium during heating without SiO_2 , but losses were negligible using SiO_2 . In the runs with SiO_2 , some fluorine was removed at or below 500°C , about three-quarters was removed at or below 675°C and all but 0.05 wt % at 850°C . However, without SiO_2 , the residual fluorine was 0.9 wt % at 850°C and 0.3 wt % at 900°C . Some of the fluorine was probably removed as SiF_4 by the SiO_2 (as reported in the UF_4 studies). But in each experiment with SiO_2 , a small amount of white film, identified by x-ray diffraction to be ammonium silicofluoride $(\text{NH}_4)_2\text{SiF}_6$, was found in cold regions of the reaction chamber. This leads to speculation that the fluorine was present in the ADU as an ammonia-uranium-fluorine compound rather than uranyl fluoride (UO_2F_2), and that silicon may replace uranium.

During preliminary experiments, it became apparent that the amount of carbon used in converting ADU to UO_2 depended somewhat on the heating cycle employed. A series of experiments employing heating rates from 3 to $30^\circ\text{C}/\text{min}$ was carried out to study this effect. The results indicated a definite trend of less carbon consumption with faster heating rates. A difference of about 0.25 wt % carbon (a C/U mole ratio of 0.09) was obtained between the slowest and the fastest rates. This difference is about 10% of the carbon used in converting ADU to UO_2 . However, duplicate runs, made in some cases, gave reasonable agreement, suggesting that it should not be difficult to obtain carbon control in the reaction. The variation in required carbon with heating rate probably occurs during reduction of a higher oxide (probably UO_3) to U_3O_8 . As the temperature is raised rapidly, some of the oxide (oxides of uranium higher than U_3O_8 thermally decompose below 580°C) decomposes before the solid state reaction with carbon can occur.

2. Conversion of ADU to UC on a Gram Scale

The results of preparing UC from ADU are given in Table 6. As mentioned previously, two heating steps were employed, i. e., a low temperature (up to 850°C) step which converts ADU to UO_2 and a high temperature step (up to 1750°C) to form the carbide. The carbide pellets produced were silvery gray in color, greatly reduced in volume over that for the original pellets, and were harder to crush than carbide synthesized from UO_2 or UF_4 . The pellets had a geometric density from 8 to 10 gm/cm³ and an immersion density (in CCl_4 at room temperature) of 11 to 12 gm/cm³. Except for Runs 10 and 11, where the amount of SiO_2 was apparently insufficient to convert all fluoride contaminant to oxide, the weight loss data indicate there is negligible uranium loss in this process.

TABLE 6
PREPARATION OF UC FROM ADU ON A GRAM SCALE

Run No.	Input* (wt %)			Reaction			Weight Loss (wt %)		Product Composition			
	Carbon	Silicon	SiO_2	Total Time (hr)	Maximum Temperature (°C)	Time at Temperature (hr)	Experimental	Theoretical†	Carbon (wt %)	Oxygen (ppm)	Silicon (ppm)	Fluorine (ppm)
Lot 1 ADU												
1	11.33	0.8	0	8	1750	2	32.0	32.2	5.04	755	180	-
2	11.10	0.8	0	8	1750	2	32.1	32.0	4.75	180	-	<20
3	10.87	0.8	0	8	1750	2	31.9	31.8	4.56	310	95	<20
4	11.56	0	1.70	6-1/2	1750	2	32.8	32.9	5.10	230	-	-
5	11.43	0	1.70	6-1/2	1750	2	33.0	32.9	4.89	460	-	-
6	11.33	0	1.70	6-1/2	1750	2	33.0	32.9	4.80	280	-	-
7	11.27	0	1.70	6	1750	2	32.8	32.8	4.70	300	<10	-
8	11.23	0	1.70	6-1/2	1750	2	33.0	32.8	4.61	185	75	<20
9	11.00	0	1.70	6-1/2	1750	2	32.9	32.7	4.44	175	135	<20
Lot 2 ADU												
10	11.20	0	0.88	5	1800	2	29.8	29.3	4.43	1540	-	-
11	11.50	0	0.88	6	1750	2	29.7	29.2	4.80	540	<10	<10
12	11.32	0	1.14	5	1800	2	29.7	29.5	4.49	400	<10	<10
13	11.60	0	1.14	6	1750	2	29.3	29.4	4.88	820	-	-
14	11.65	0	1.76	6	1750	2	30.1	30.0	4.92	720	-	-

*Remainder is ADU.

†Based on a pure uranium carbide product with no loss of uranium in the reaction

-No analysis.

Best results were obtained using about 0.65 wt % SiO_2 for each 1 wt % fluorine. Fluorine analysis indicated the carbide products were essentially free of fluorine. Silicon metal also appears to be quite effective in removing fluorine and preventing uranium loss.

Figure 3 illustrates the product carbon content as a function of carbon input. These results indicate that a predetermined product can be readily produced from ADU. Based on this data, the mole ratio of carbon to uranium required in this process to produce $\text{UC}_{1.0}$ with Lot 1 ADU was about 3.5, using 1.7 wt % SiO_2 ; 3.4, using 0.8 wt % Si; and was about 3.4 with Lot 2 ADU using SiO_2 . A possible equation for the overall conversion of ADU (neglecting fluoride) to UC would be

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Figure 3. Carbon Content of UC, Prepared from ADU on a Gram Scale, as a Function of Carbon Input

The low residual oxygen contents that were obtained for the hypostoichiometric UC provide one very significant feature of the results. Normally, at these temperatures, carbide prepared by carbothermic reduction of UO_2 contains sufficient oxygen to replace missing carbon in the UC lattice. As reported in the UF_4 study, residual silicon (not all was used in removing fluorine) is believed to have aided in obtaining the low oxygen contents by action similar to that of a platinum flux in the vacuum fusion analysis for oxygen in metals. This low residual oxygen content, <300 ppm, would be a definite advantage of this process in producing carbide melt stock for arc-melting into fuel slugs since gas evolution and electrode erosion, which complicate carbon control during arc-melting, would be minimized with high quality melt stock.

The data for experiments to determine the effect of using different silicon inputs in the ADU conversion are given in Table 7. As expected, the results indicate a considerable loss of uranium in the first two runs where a low silicon input was used, reasonably similar results in Runs 3 and 4, and residual silicon in products of Runs 5 and 6 where excess silicon was used. From a standpoint

TABLE 7
CONVERSION OF ADU TO UC WITH DIFFERENT
AMOUNTS OF SILICON

Run No. *	Silicon Input† (wt %)	Weight Loss (wt %)		Product Composition		
		Experimental	Theoretical§	Carbon (wt %)	Oxygen (ppm)	Silicon (ppm)
1	0	37.1	31.4	5.55	1070	0
2	0.4	34.2	31.4	5.14	1290	<10
3	0.8	31.9	31.8	4.79	420	<10
4	1.0	31.6	31.8	4.82	<100	15
5	2.0	31.5	32.5	4.84	180	5900
6	4.0	32.0	34.0	5.04	535	8800

*Reaction Conditions: 6 to 7 hours total heating time with 2 hours at the maximum temperature of 1750°C

†Tests were made using ADU Lot 1, and a ratio of 0.1253 gm C/gm ADU was used in each run.

§Assuming a $\text{UC}_{1.0}$ product, no uranium loss and vaporization of all silicon.

of carbon control, low residual oxygen, and low silicon content, a silicon input of about 1 wt % appears to yield the best carbide product. This is equivalent to about 0.4 wt % Si for each 1 % F in the ADU.

Experiments carried out to compare the quality of UC prepared from ADU at finishing temperatures from 1450 to 1800°C indicated negligible difference in reaction completion (as evidenced by residual oxygen content) at temperatures from 1650 to 1800°C, but a significant trend of less complete reaction at lower temperatures. The residual oxygen contents of ≤ 500 ppm at temperatures of $\geq 1650^\circ\text{C}$ are lower than normally obtained in preparing UC from UO_2 under these same conditions. However, as mentioned previously, the better results with ADU may be caused by the action of the Si or SiO_2 additive.

3. Conversion of ADU to UC on a Kilogram Scale

Data for the kilogram scale conversion of ADU to UC are given in Table 8. Heats 1 to 3 were made using a three-crucible assembly where each crucible

TABLE 8
PREPARATION OF UC FROM ADU ON A KILOGRAM SCALE

Heat No. *	Input† (wt %)		Reaction			Weight Loss (wt %)		Expected Carbon (wt %)	Product			
	Carbon	SiO ₂	Total Time (hr)	Maximum Temperature (°C)	Time at Temperature (hr)	Experimental	Theoretical§		Carbon (wt %)	Oxygen (ppm)	Silicon (ppm)	Fluorine (ppm)
2-kg Runs												
1A	11.03	1.14	8	2050	4	29.0	29.6	4.25	4.23	250	75	-
B	11.33	1.14	8	2050	4	28.8	29.5	4.50	4.46	455	<10	-
C	11.75	1.14	8	2050	4	28.5	29.4	4.75	4.83	470	<10	-
2A	10.90	1.14	7-3/4	2000	2	-	-	4.40	4.32	315	-	-
B	11.33	1.14	7-3/4	2000	2	-	-	4.65	4.67	425	<10	-
C	11.09	1.74	7-3/4	2000	2	-	-	4.50	4.51	870	-	-
3A	10.90	1.14	7-1/4	2050	3	32.6	32.1	4.40	4.36	<100	125	<10
B	11.33	1.14	7-1/4	2050	3	32.0	32.0	4.65	4.59	<100	100	<10
C	11.09	1.74	7-1/4	2050	3	32.4	32.6	4.50	4.50	130	75	-
20-kg Runs												
4	11.40	1.14	9	2050	3-2/3	31.6	32.0	4.70	5.16	<100	<10	-
5	11.08	1.14	10	2050	4	32.3	32.0	4.75	4.80	160	20	<10
6	10.88	1.14	10	2050	4	32.4	32.0	4.60	4.58	<100	10	-

*Heat 1 contained pellets without binder, the remaining heats consisted of agglomerates containing about 1 wt % PVA and about 3 wt % water.

†Remainder was Lot 2 ADU

§Based on uranium content of ADU, a pure UC product, no loss of uranium in reaction, and - for Heats 2 to 6 - agglomerates containing 1 wt % PVA and 3 wt % H_2O .

-No analysis.

could hold over 2 kg of charge. The typical carbide product was a silvery gray color quite similar in appearance to that produced by carbothermic reduction of UO_2 under these conditions. During reaction, the pellets and agglomerates were reduced in volume by a factor of about three and were sintered into clusters which were easily separated into individual pieces.

These results demonstrate that UC of low oxygen content, and ranging in composition from hypostoichiometric to hyperstoichiometric, can be prepared on a kilogram scale from ADU. These oxygen contents are similar, if not lower, than those normally achieved in the production of UC melt stock by carbothermic reduction of UO_2 . The preparation of carbide melt stock with low oxygen content is important since use of this carbide will improve composition control during melting and casting of slugs. Results of runs 1A, 2A and 3A, in which carbon contents are in the range of 4.2 to 4.4 wt %, are also quite encouraging because the use of this hypostoichiometric carbide as melt stock would reduce or eliminate the addition of uranium metal in the subsequent arc-casting process. The low residual fluorine and silicon content indicates nearly complete removal of these elements.

The kilogram scale preparations of UC required much higher finishing temperatures, 2000 to 2050°C, than the gram scale experiments. (Kilogram scale reductions carried out at 1950°C were not completed even after a holding time of 5 hours.) This may have been influenced by the low carbon contents, 4.5 wt % C, in many of these runs. However, the higher temperatures (and longer hold times) required are probably associated with the larger charge and the fact that the finishing pressure in the kilogram runs was about 20 μ , a factor of 100 higher than the gram scale finishing pressure. Since the equilibrium pressure of CO over UO_2 and graphite is a function of temperature, $\log P_{(\text{atm})} = 9.576 - \frac{19,740(14)}{T(^{\circ}\text{K})}$, it is evident that a lower finishing pressure would permit completion of this reaction at reduced temperature.

The weight loss data for the pellets suggest that negligible uranium loss occurs in the carbothermic reduction of ADU to UC even at these high temperatures. Uranium loss was more difficult to evaluate by weight loss data with agglomerates since these contained PVA and a variable amount of water (approximately 3 wt %) depending on the agglomerate drying efficiency. There were no deposits noted and identified as uranium on the crucible cover or in the furnace chamber.

Comparison of the results obtained with the pellets and the agglomerates indicates that a slightly longer reaction time was required with the pellets. When binder was used, less carbon was required for the same product carbon content, indicating binder contributes a significant amount of carbon to the reaction. This effect was expected since it has been observed during the carbo-thermic reduction of U_3O_8 .⁽¹⁰⁾ However, the general agreement in the expected carbon and the observed carbon content of these products indicates that the behavior of binder is reasonably reproducible in this reaction.

The expected carbon content for Heat 4 was based on the results of the 2-kg runs. The actual carbon content for Heat 4 was much higher than predicted. The reason for this is not definitely known but was probably associated with a difference in reduction of ADU to UO_2 with different size batches, or a difference in carbon pickup with different hold times and charge sizes. The results of Heats 5 and 6, however, indicate that a predetermined composition can be obtained on a production basis. The carbon content of UC prepared from ADU on a kilogram scale is plotted as a function of carbon input in Figure 4. It is evident from Figure 4 that the results were consistent and that carbide of any desired carbon composition can be produced in kilogram quantities. The preparation of carbide with 4.80 wt % C from this ADU required a carbon input of 11.08 wt % for the agglomerates on a 20-kg scale, 11.54 wt % for agglomerates on a 2-kg scale, and 11.72 wt % for pellets without binder on a 2-kg scale.

The 10-hour heat cycle used to convert 20 kg of ADU is longer than the 6-hour cycle used for the conversion of UO_2 to UC in this same furnace. Of course, about double the amount of gas must be handled with ADU than in the UO_2 reaction, so that a longer heat cycle would be expected. However, the ADU heat cycle could easily be reduced with increased pumping capacity.

A thin, white-colored film was observed on the furnace chamber wall (it formed during the low temperature, $<900^\circ\text{C}$, part of the heat cycle) after each of the kilogram scale conversions. This deposit was analyzed by x-ray diffraction and found to be ammonium silicofluoride $[(NH_4)_2 SiF_6]$. The deposit was easily removed after each heat using a brush attachment with a commercial vacuum cleaner.

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Figure 4. Carbon Content of UC, Prepared from ADU on a Kilogram Scale, as a Function of Carbon Input

After each 20-kg scale heat, a coagulate was observed when the vacuum pump oil was changed. Analyses revealed that this substance was ammonium fluo-ferrate $[(\text{NH}_4)_3 \text{Fe F}_6]$ and ammonium silicofluoride $[(\text{NH}_4)_2 \text{SiF}_6]$. It is theorized that this material formed during the reaction and was swept into the pump with the reaction product gases. This material could in time be harmful to the pump and undoubtedly would reduce the pumping rate. For future production of UC from ADU, it would be recommended that some means of removing condensates (such as a baffle, cold trap or chemical trap) be incorporated into the reaction gas line ahead of the pump.

The conversion of ADU could be carried out in two steps using two furnaces (as in the gram scale experiments) instead of a single furnace for the entire

reaction. In that case, the low temperature (<900°C) conversion of ADU to UO_2 , which removes binder and generates undesirable condensates, could be carried out in a resistance furnace using a very rough vacuum or an inert gas flow. The final reaction to UC, where a clean system is advantageous, could be completed in much less time using an induction furnace system identical to that commonly used in the UO_2 -C reaction.

C. UO_3 STUDIES

1. Conversion of UO_3 to UO_2

As in the previous studies, the initial experiments were carried out to investigate conversion of the uranium compound to UO_2 . Data for the tests with UO_3 are given in Table 9. In these tests, reaction began slowly at $\sim 250^\circ\text{C}$, increased somewhat at $\sim 450^\circ\text{C}$, and was quite rapid at $\sim 700^\circ\text{C}$. These results

TABLE 9
CARBOTHERMIC REDUCTION OF UO_3 TO UO_2 IN VACUUM

Run No.	Input*		Reaction		Product Composition			Carbon Reacted
	mole ratio (C/ UO_3)	carbon (wt %)	Temperature ($^\circ\text{C}$)	Time (hr)	Uranium (wt %)	O:U Ratio	Carbon (wt %)	mole ratio (C/ UO_3)
1	3.50	12.82	500	4	72.0	2.83	12.17	0.21
2	3.50	12.82	675	3-1/2	73.9	2.58	12.00	0.30
3	3.50	12.82	850	4	76.8	2.01	11.69	0.53

*The carbon input is near that expected for conversion of UO_3 to UC.

indicate that, in general, the conversion occurs by carbothermic reduction rather than by thermal decomposition. About 1/2 mole carbon is consumed in the reduction of UO_3 to UO_2 . The reaction is represented as

2. Conversion of UO_3 to UC

Data for the preparation of UC from UO_3 are given in Table 10. Again two heating steps were employed, i. e., conversion to UO_2 at $<850^\circ\text{C}$ and formation

TABLE 10
PREPARATION OF UC FROM UO_3 BY CARBOTHERMIC
REDUCTION IN VACUUM

Run No.	Input			Reaction			Weight Loss (wt %)		Uranium Carbide Product		
	Carbon		SiO_2 (wt %)	Total Time (hr)	Time at Temperature (hr)	Maximum Temperature ($^{\circ}\text{C}$)	Experimental	Theoretical*	Carbon (wt %)	Oxygen (ppm)	Silicon (wt %)
	mole ratio (C/UO_3)	(wt %)									
1	3.45	12.65	0	9	3	1750	25.2	24.9	4.57	660	-
2	3.50	12.81	0	9	3	1750	25.2	24.9	4.73	760	-
3	3.54	12.94	0	9	3	1750	25.2	24.9	4.80	435	-
4	3.58	13.07	0	8-1/2	2-1/4	1750	24.8	24.9	5.05	625	-
5	-	12.58	1.00	8-1/2	2-1/4	1750	26.0	25.8	4.45	150	0.10
6	-	12.76	1.00	8-1/2	2-1/4	1750	26.2	25.8	4.67	405	0.01
7	-	12.95	1.00	8-1/2	2-1/4	1750	26.0	25.8	4.87	165	0.10

*Calculation based on uranium content of the UO_3 (82.0 wt %), no loss of uranium, and a pure UC product.

-No analysis.

of carbide above 1300°C . The UC pellets were silvery gray in color, as in the preparations from UF_4 and ADU, and had geometric densities of 7 to 8 gm/cm^3 and immersion densities (in CCl_4 at room temperature) of 11.0 to 11.5 gm/cm^3 .

SiO_2 was used as an additive in some of the runs. Comparison of the results indicate that it is effective in obtaining a UC product with a low residual oxygen content. The reason for this effect, as explained in the UF_4 and ADU studies, is believed to be the fluxing action of silicon. In most cases, these products contained some residual silicon.

The product carbon content is plotted as a function of carbon input in Figure 5. These data indicate that carbide of controlled carbon content can be readily prepared from UO_3 using a two-step heating cycle. About 3.5 moles of carbon are needed in preparing UC from UO_3 . The reaction is:

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Figure 5. Carbon Content of UC, Prepared from UO₃ as a Function of Carbon Input

IV. ECONOMIC COMPARISON OF RAW MATERIALS

A brief economic study with regard to uranium raw materials was carried out after the technical feasibility of preparing uranium carbide from UF_4 , ADU and UO_3 was established. The two current sources of enriched uranium are the gaseous diffusion plant and the fuel reprocessing plant. The costs of feed material from each source will be discussed separately.

The nominal cost of obtaining quantity lots of UO_2 from low enrichment UF_6 (the diffusion plant product) is about \$8/kg U. Comparative estimates indicate the cost for UF_4 is about 1/2 and for ADU is about 3/4 of this cost. Providing the uranium source is UF_6 , UF_4 is recommended as being the most economical of these three raw materials. The use of UF_4 rather than UO_2 for carbide preparation has the potential of saving up to \$4/kg U.

When the uranium source is a reprocessing plant where uranyl nitrate is the product, both ADU and UO_3 are recommended as being more economical raw materials than UO_2 . Comparative cost estimates indicate that low enrichment ADU and UO_3 can be obtained for about \$2/kg U less than UO_2 . However, UF_4 would be the more economical raw material for carbide preparation, provided that the reprocessing plant employs the fluoride volatility method.

The overall cost (including uranium raw material) of preparing UC via carbothermic reduction of UO_2 in production lots is about \$25 to 30/kg U. Therefore the potential savings of \$2 to 4/kg U by using UO_3 , ADU or UF_4 represents from about 7 to 14% of the total preparation cost.

It must be recognized that the savings mentioned for these raw materials are ultimate values and that a savings may not be realized in actual practice. For example, the experimental work has shown that a longer heat cycle (over the UO_2 process) is required with these materials, i. e., a higher production labor cost. Also, the cost of additional raw materials (graphite and SiO_2) although minor, must be included. Analytical costs would also be increased with these materials since analyses for silicon and fluorine would be needed when using UF_4 and ADU.

The use of reprocessed uranium appears particularly attractive for the HWO CR since low enrichment fuel, 1 to 2% U^{235} , is required and a supply of

suitably enriched uranium, i. e., spent fuel from a light water reactor expected to have a U^{235} content from 1.0 to 1.6%, should be available. Uranium from a reprocessing plant would be considerably cheaper than an equivalent amount of uranium (no matter which raw form is considered) from the diffusion plant. Use of reprocessing plant uranium directly rather than recycling to the diffusion plant would eliminate conversion to UF_6 , diffusion plant separative costs and re-conversion of UF_6 to a uranium form suitable for carbide preparation. The potential cost saving is the sum of the conversion costs from uranyl nitrate to UF_6 , and UF_6 to the raw material for carbide preparation, less the cost of converting uranyl nitrate to ADU or UO_3 . Using current costs, and including shipping charges, processing losses, and use charges, the savings could be up to \$12/kg U. It should be noted that this savings includes an estimate of the difference between the price of uranium from a diffusion plant and the expected market value of uranium from a reprocessing plant. Although reprocessed uranium with the fission products removed may contain a small amount of other uranium isotopes, U^{236} and U^{234} , no difficulty is expected in the subsequent carbide preparation. Another advantage of using reprocessed uranium in the HWO CR is that it would eliminate the cycling of uranium containing U^{236} through the diffusion plant (the separation of U^{235} from U^{236} being more costly than the separation of U^{235} from U^{238}).

It is quite likely that the enrichment available from the reprocessing plant will be slightly different than the HWO CR requirements. However, slight adjustments in fuel enrichment could be made by blending in diffusion plant uranium or natural uranium depending on desired enrichment. Blending could be accomplished during the carbon mixing operation to minimize processing steps.

Of course, discretion and planning would be required to carry out a fuel fabrication program relying on this uranium source. The success of this approach would depend on the enrichment, quantity and availability of reprocessed fuel when needed. In general, the optimum procedure would be to integrate fuel requirements for an HWO CR concept with spent fuel or scrap recovery for other specific reactors so that accurate predictions of available uranium and specific enrichment could be determined.

V. CONCLUSIONS

Uranium carbide of controlled carbon content can be prepared from UF_4 , ADU and UO_3 by solid state reaction. Although intermediate stages are involved, the probably overall reactions are,

A small amount of Si or SiO_2 blended with the reactants in the ADU conversion successfully removed the fluorine contaminant in ADU without uranium loss.

The production of UC from ADU on a 20 kg scale was demonstrated using essentially the same physical operations employed in converting UO_2 to UC. Although a longer heating cycle was necessary in the conversion of ADU, compared to UO_2 , the reaction time could be reduced with increased pumping capacity. Uranium carbide of high quality suitable for use as melt stock in an arc-melting and casting process was prepared. The method of using UF_4 and UO_3 also appears adaptable for large-scale UC production.

An economic comparison of enriched uranium materials suitable for preparing UC indicates that the potential saving is highest using,

- 1) UF_4 from a diffusion plant source.
- 2) ADU and UO_3 from a reprocessing plant source which employs the solvent extraction process.
- 3) UF_4 from a reprocessing plant source which employs the fluoride volatility process.

The use of reprocessed uranium, originating as spent light water reactor fuel, appears particularly attractive for the fabrication of HWOCR fuel since the U^{235} enrichment is expected to be near that required in the HWOCR. Taking into account the higher production costs arising from the longer heat cycle and additional analyses, a cost reduction with UO_3 and ADU is considered marginal but may be possible with UF_4 . Development of the UF_4 process on a kilogram scale

is recommended to resolve process parameters and to establish actual processing costs.

In view of the successful results obtained in the UF_4 studies, it can be speculated that other nuclear fuel fluorides, such as plutonium fluoride or thorium fluoride, could be converted to oxide or carbide using the method developed here. Mixtures of these fluorides with uranium fluoride could also be converted. Based on the success in the ADU studies, plutonium hydroxide (normally precipitated from plutonium nitrate by ammonia) and mixtures of plutonium hydroxide and ADU should be readily converted to carbide. These methods should prove economical for mixed carbide preparation.

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