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STUDIES OF THE PREPARATION OF MIXED CARBIDE FUEL UTILIZING COPRECIPITATION

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RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

Work Performed Under
Contract No. AT(30-1)-3713
With the United States Atomic Energy Commission
by The Carborundum Company
Research and Development Division
Niagara Falls, New York

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QUARTERLY PROGRESS REPORT NO. 2
September 1, 1966 through November 30, 1966

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FOREWORD

This project is part of the AEC Fuel Cycle Development Program. The work was performed in the Nuclear Fuels Department of the Research and Development Division of The Carborundum Company at Niagara Falls, New York. K. M. Taylor is the project manager and C. H. McMurtry is the project engineer. In addition to the authors, C. J. Boos and T. J. Keaty contributed to the work described in this report.

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I. INTRODUCTION

The coprecipitation of carbon and metal bearing compounds from a common solvent is a new approach to the process of making refractory metal carbides. This method has been successfully applied at The Carborundum Company to the synthesis of several refractory metal carbides including preliminary work on UC. The object of this work is to extend this technology to the preparation of (U,Pu)C fuels.

In order to produce power from fast reactors on a basis competitive with that from thermal reactors it is necessary to achieve further economies in the fast reactor fuel cycle. It is believed that this process will result in savings in the carbide fuel cycle for several reasons. Stoichiometric (U,Pu)C may be made more consistently by the proposed process because of the very intimate and homogeneous mixture of the reactants and it is believed that a stoichiometric fuel will make possible maximum burnups with retention of fission products. Also, stoichiometric fuel is desirable when using a sodium bond, which in turn is necessary for operation at maximum specific power. Furthermore, since this procedure will permit the use of nitrate solutions as a U,Pu source rather than the oxide or metal, the method is believed to be consistent with more economical fuel processing.

Initial work during the first quarter indicated that a single phase UC could be prepared by coprecipitation of the metal and carbon bearing constituents from a uranyl nitrate-sucrose solution. However, the reproducibility of these early experiments was poor and the process variables causing this difficulty were not well understood.

II. SUMMARY

This report describes the synthesis of (U,Pu)C using a coprecipitation process as well as further study of the process variables affecting the reproducibility of this method. Synthesis of UC was used as a model to study process variables and develop background information relative to the preparation of (U,Pu)C prior to initiating work with this compound. This study of process variables has included development of apparatus to carry out coprecipitation, dehydration and initial decomposition of the coprecipitate. The effects of time, temperature and atmosphere during this stage were evaluated.

Summary of this quarter's work is as follows:

1. An apparatus and procedure were developed for carrying out the initial stages of this process. This included coprecipitation by evaporation, condensation of the acid fumes, dehydration and decomposition of the coprecipitated reactants in a controlled atmosphere to 600°C.

2. Non-uniform heating rates up to 600°C were identified as the process variable resulting in poor reproducibility in the final carbide product.

3. Automatic control of the rate of temperature rise to 600°C resulted in good reproducibility in carbide synthesized from uranyl nitrate-sucrose solutions. The success of this technique can be seen in the analyses of three duplicate carbide products which had total carbon contents of 6.94, 7.02 and 6.93 percent, respectively.

4. Synthesis of $(U_{0.8}, Pu_{0.2})C$ was carried out using the apparatus and procedure developed during the study of process variables.

5. Two additional organic compounds, furfural and phenyl-formaldehyde resin, were evaluated as sources of carbon.

III. PROCEDURE

A procedure was adopted which consisted of three distinct stages:

1. Preparation of reactants.

2. Coprecipitation, dehydration and initial decomposition.

3. Reaction to form carbide.

The first stage, preparation of reactants, involved the solution of sucrose, 5 to 8 g, in 50 ml of an analyzed nitrate solution. The concentration of the U or U,Pu in these nitrate solutions was approximately 0.15 g/ml.

Coprecipitation, dehydration and initial decomposition were carried out in a single step. This was accomplished in a standard glass reaction kettle fitted with a heating mantle, thermocouple, condenser and gas inlet. In this manner the acid fumes could be condensed and an enclosure was provided in which a controlled atmosphere could be maintained. A cam type controller was used to program the heating cycle up to 600°C. This cycle included a two hour hold at 120°C to evaporate and coprecipitate the reactants, followed by a rise in temperature of 100°C per hour to 600°C and finally a hold at this temperature for 13 hours. At the end of this 20 hour period heating was terminated and the residue cooled to room temperature.

The dried residue was pelletized for ease of handling and in the case of UC, synthesis was carried out in a molybdenum boat in an alumina tube muffle furnace in an argon atmosphere. The (U,Pu)C syntheses were carried out in molybdenum boats in a graphite resistance furnace with a helium atmosphere. The temperature, in both cases, was raised at a rate of 1000 to 1500°C per hour to 1700°C and held for five hours.

Finished carbides were unloaded from the reaction furnace directly into a glovebox with a high purity inert atmosphere for sampling. Evaluation of the carbide product included x-ray determination of the phases present, and the (U,Pu)C lattice parameter as well as analysis for the total carbon content.

IV. PROCESS VARIABLES

A. Coprecipitation and Heat Treating to 600°C

Of primary concern this quarter were the process variables which affect the reproducibility of this coprecipitation process for making carbides. Previous work indicated that the yield of carbon from the sucrose and perhaps the oxygen content of the oxide from the nitrate varied due to non-uniform conditions during coprecipitation and heat treating to 600°C (see Table VIII Quarterly Progress Report No. 1). Experiments in which these three operations were carried out in a single step in a glass reaction kettle also indicated a lack of reproducibility on heating to 600°C. Table I, experiments 1 through 6, shows the extent of variation in the total carbon content after heating to 600°C. As can be seen, a similar variation occurred in the carbide product after heating to 1700°C. This variation which was greater than ± 1% from the mean, i.e., from 4.83 to 7.17 percent total carbon, appeared to be a result of non-uniform heat treatment at low temperatures. For this reason a cam-type program controller was used to provide automatic control of the heating up to 600°C. This program, described in the Section II, Procedure, resulted in improved reproducibility. As can be seen in experiments 8 through 10, Table I, the variation in total carbon was from 6.93 to 7.02 percent or less than ± 0.1 percent from the mean.

B. Uranyl Nitrate-Sucrose Ratio

The uranyl nitrate-sucrose ratio required to produce a particular carbon content, such as stoichiometric UC, has been shown to vary depending upon a number of factors. These include the acidity of the nitrate solution and the conditions of coprecipitation, dehydration and low temperature decomposition of the coprecipitate. Thus in most experiments during this quarter no attempt was made to adjust the uranyl nitrate-sucrose ratio until those factors affecting reproducibility were under control. Two experiments were carried out with a reduced sucrose content, as shown in experiments 11 and 12 in Table I. The expected response to the reduced sucrose content was achieved and, in addition, the duplication of these results further confirms the reproducibility which can result from careful control of heating during the early stages of reaction.

The low temperature heat treatment of the coprecipitated reactants will affect the oxygen content of the oxide and the yield of carbon from the reactants and thus alter the required uranyl nitrate-sucrose ratio. It would be desirable to reduce the nitrate to a dioxide and the sucrose to carbon at as low a temperature as possible and prior to the start of the UO_2-carbon reaction. Preferably this should be accomplished below 600°C, the temperature limit of the glass kettle used in the evaporation, coprecipitation and low temperature heat treating. Chemical analysis of the coprecipitated reactants after heating to 600°C in nitrogen indicated that this had not occurred, that is the total carbon and uranium as UO_2 were less than 100 percent as seen in Table I. Whether this was incomplete reduction of the oxide or only partial decomposition of the sucrose could not be determined by analysis of the complex product.

TABLE I

$UO_2(NO_3)_2 \cdot 6H_2O$ - Sucrose Reaction Product After Heating to 600°C and 1700°C*

Exp. No.	Sucrose in Reactants, wt.%	After Heating to 600°C: Uranium as UO_2, wt.%	After Heating to 600°C: Total Carbon, wt.%	After Heating to 1700°C: Total Carbon, wt.%	Remarks
1	28.57	85.76	13.38	6.00	Manual temperature control to 600°C
2	"	85.61	11.88	4.83	"
3	"	83.15	12.20	5.03	"
4	"	84.06	14.28	7.17	"
5	"	84.27	13.50	6.56	"
6	"	83.81	12.96	6.76	"
7	"	83.83	13.41**	6.82	Automatic temperature control to 600°C
8	"	84.15	13.66	6.94	"
9	"	82.92	13.38	7.02	"
10	"	84.27	13.39	6.93	"
11	26.76	-	12.20	5.28	"
12	"	-	22.25	5.38	"

*A nitrogen atmosphere was used to 600°C and an argon atmosphere during final synthesis at 1700°C for five hours.

**The rate of temperature rise used in this experiment was modified slightly before running the three duplicates 8, 9 and 10 or the two duplications in 11 and 12.

UO_3 can be readily reduced in hydrogen to UO_2 at temperatures of 500°C or higher(1), thus three experiments were carried out in which the coprecipitated reactants were heat treated to 600°C in hydrogen. The erratic data from these experiments (Table II) were thought to be the result of the manual control of the rate of heat-up rather than an effect of the hydrogen. However, Table II, indicates that the reactants had still not been completely reduced to UO_2 and carbon and that the yield of carbon was significantly lower in hydrogen.

TABLE II

$UO_2(NO_3)_2 \cdot 6H_2O$ - Sucrose Reaction Products After Coprecipitation and Heating to 600°C in Hydrogen*

Exp. No.	Composition of Reaction Product, wt.% Total Carbon	Nitrogen	Uranium as UO_2
1	11.03	0.11	83.6
2	9.87	-	87.8
3	10.54	-	87.9

*Manual control of the rate of temperature rise was employed in these experiments.

Since it was difficult to evaluate the degree decomposition or the yield of carbon from sucrose in the heat treated coprecipitate, several experiments were carried out in which sucrose alone was decomposed. The conditions were similar to those employed in the synthesis experiments with the coprecipitated uranyl nitrate and sucrose. Results of these experiments are shown in Table III and indicate that the decomposition of sucrose was complete only at a temperature of 1200°C in nitrogen and at 800°C in hydrogen. Three experiments were also carried out in an atmosphere of 90 percent nitrogen - 10 percent hydrogen, a less hazardous reducing atmosphere which could be used in a glovebox operation. This atmosphere appeared less effective than pure hydrogen but probably would give comparable results with higher gas flow rates. This work indicated that hydrogen atmospheres would be helpful in reducing the temperature required to decompose sucrose to 100 percent carbon and thus contribute to better control of the process.

V. (U,Pu)C SYNTHESIS

Synthesis of (U,Pu)C was initiated during this quarter and the procedure employed was similar to that used in the preparation of UC while studying process variables. Only two minor differences existed in the experimental conditions. The plutonium nitrate solution had a H+ molarity of 3.18 thus the U,Pu nitrate solution was more acid than the uranyl nitrate solution alone. The previous work on the effect of acidity indicated that a lower yield of carbon would result as the acidity increased but would not otherwise alter the reaction product. The second difference was in the final reaction conditions. In this stage reaction was carried out in a graphite resistance furnace in helium although the reactants were contained in a covered molybdenum boat as in previous work. This variation was not expected to affect the course of reaction.

The uranyl nitrate and plutonium nitrate solutions were mixed to yield a 4/1 ratio of U to Pu. The plutonium nitrate solution was prepared by dissolving plutonium metal in nitric acid and obtained

TABLE III

Effect of Temperature and Atmosphere on the Decomposition of Sucrose*

Exp. No.	Atmosphere	Temperature, °C	Residue, wt.%	Total Carbon In Residue, wt.%
1	Nitrogen	200	76.30	50.24
2	"	300	40.98	69.80
3	"	400	29.79	82.64
4	"	500	25.88	91.79
5	"	500	25.19	97.25
6	"	500	25.54	91.38
7	"	600	24.62	93.34
8	"	700	23.77	95.99
9	"	800	23.17	96.58
10	"	1000	21.90	97.33
11	"	1200	18.00	100.17
12	Hydrogen	400	26.14	87.87
13	"	600	20.29	97.87
14	"	800	17.80	100.04
15	90 H_2 - 10 N_2	400	30.23	86.23
16	"	600	23.59	94.60
17	"	800	21.90	97.49

*In each experiment 6 g of sucrose was heated to the indicated temperature at a rate of 100°C per hour and held at temperature for 16 hours. Automatic control of the rate of temperature rise was employed in all experiments.

from Isochem Inc. at Richland, Washington. Analysis supplied with this solution is shown in Table IV.

In the first two experiments the sucrose to U,Pu nitrate ratio was similar to that in UC synthesis experiments Nos. 11 and 12 in Table I. As expected, the total carbon in the product after synthesis at 1700°C was lower than in the comparable UC synthesis, because of the higher acidity in the U-Pu nitrate solution. The

TABLE IV

Analysis of Plutonium Nitrate Solution*

Plutonium Concentration	0.2309 g/ml
Specific Gravity	1.406
H+ Molarity	3.18 M
U	52 ppm
F	62 ppm
Cl	142 ppm

Metallic Impurities, ppm

Ag	1	Cu	2	Ni	20
Al	5	Fe	195	P	<1
As	<20	Ge	<5	Pb	2
B	2	K	<5	Si	41
Be	<1	Li	<5	Sn	10
Bl	<1	Mg	5	Ti	10
Ca	10	Mn	5	Tl	<1
Cd	<10	Mo	<5	V	<100
Cr	20	Na	20	Zn	<5

Isotopic Analyses, wt.%

Pu 239	91.038	Pu 240	8.128
Pu 241	0.799	Pu 242	0.035

*Supplied by the Plutonium Finishing Section, Isochem Inc., Richland, Washington.

results of these two duplicates are shown in Table V. X-ray identification of the phases present indicated two (U,Pu)C type phases to be present but in spite of the low total carbon content no dioxide type phases were detected. It seems probable that significant amounts of oxygen were present in this product as oxycarbide. The low values which were obtained for the lattice parameter also indicated that the material was an oxycarbide. The two (U,Pu)C type phases probably arise from a surface layer having a slightly different oxygen content than the bulk and thus resulting in oxycarbides with slightly different lattice parameters.

Two additional synthesis experiments were carried out in which the sucrose content was adjusted to yield a total carbon content near or slightly in excess of the stoichiometric value for (U,Pu)C. These experiments, Nos. 3 and 4, Table V, resulted in hyperstoichiometric carbides. To date insufficient experiments have been carried out to provide a statement of the reproducibility of the (U,Pu)C reaction product but no unusual behavior was noted in these first four syntheses.

TABLE V

(U,Pu)C Reaction Product after Synthesis at 1700° for Five Hours*

Exp. No.	Sucrose** in Reactants, wt.%	Total Carbon, wt.%	X-ray Analysis - Phases
1	41.6	3.76	-
2	41.6	3.76	2 (U,Pu)C type phases - major
3	46.64	6.20	(U,Pu)C type - strong; UC_2 - weak to moderate; U_2C_3 type - faint
4	44.2	5.00	(U,Pu)C type - major UC_2 - faint

*Automatic control of the rate of temperature rise to 600°C was employed in these experiments.

**Based on the weight of sucrose and the weight of elemental U,Pu present.

VI. OTHER ORGANICS AS A SOURCE OF CARBON

Two additional materials were evaluated as potential sources of carbon for use in the coprecipitation process for making carbide. These were phenylformaldehyde resin and furfural. Phenylformaldehyde resin is a thermal setting material with a normally higher carbon value than sucrose. Furfural[2], when contacted with HCl or dilute H_2SO_4, forms a gelantinous mass which can be converted to carbon on subsequent heating.

In the work with phenylformaldehyde resin, uranyl nitrate solution was mixed with the resin and this mixture cured at 180°C for 16 hours to polymerize the resin. In the second experiment, furfural was mixed with the uranyl nitrate solution and dilute H_2SO_4. The resulting mixture was allowed to gel overnight at room temperature. Both the cured resin and furfural gel were then treated in the same manner as the uranyl nitrate-sucrose solutions and heated to 600°C. The analysis of the residues at this point are shown in Table VI. Both of these sources of carbon look promising at this stage.

VII. FUTURE WORK

During the next quarter primary efforts will be on producing stoichiometric (U,Pu)C from the mixed U,Pu nitrate solutions and sucrose. In addition sufficient synthesis experiments will be carried out to provide an accurate statement of the reproducibility of this process. The (U,Pu)C product will be characterized by chemical and x-ray analyses and by metallography on sintered pellets.

An investigation of sintering per se, however, will not be carried out during the next quarter. A final report will be prepared by the end of the next quarter summarizing the results of the study of the preparation of (U,Pu)C utilizing coprecipitation.

TABLE VI

Other Organics as a Source of Carbon

Exp. No.	Organic Compound	Organic in Reactants, wt.%	Composition of Reaction Product After Heating to 600°C in N_2, wt.%		
			Carbon	Nitrogen	Uranium
1	Phenylformaldehyde Resin	78.5	12.74	<0.01	73.1
2	Furfural $C_4H_2O \cdot CHO$	31.6	8.00	<0.01	77.9
3	Sucrose $C_{12}H_{22}O_{11}$	28.5	14.2	0.42	71.15

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