NDA 2162-3

CARBIDE FUEL DEVELOPMENT

Progress Report

Period of February 1, 1961 to April 30, 1961

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DISCLAIMER

FOREWORD

The Carbide Fuel Development project is part of the AEC Fuel Cycle Development Program. The prime contractor is the Nuclear Development Corporation of America (NDA), and the subcontractor is The Carborundum Company. NDA is performing the conceptual design, fuel evaluation, fuel irradiation, and irradiated fuel reprocessing. The Carborundum Company is fabricating the fuel. Both companies have built plutonium handling facilities.

This report covers progress from February 1, 1961 to April 30, 1961. Previous progress was reported in:

NDA 2140-2, Carbide Fuel Development – Phase I Report (Oct. 15, 1959)
NDA 2145-1, Carbide Fuel Development – Progress Report (Mar. 11, 1960)
NDA 2145-4, Carbide Fuel Development – Progress Report (June 13, 1960)
NDA 2145-5, Carbide Fuel Development – Progress Report (Aug. 30, 1960)
NDA 2145-6, Carbide Fuel Development – Phase II Report (Nov. 6, 1960)
NDA 2162-1, Carbide Fuel Development – Progress Report (Feb. 28, 1961)

CONTENTS

TABLES

1. INTRODUCTION

Fuel made of a combination of UC and PuC has a potential of reducing the fuel cycle cost of existing fast breeder reactors. The fuel cycle cost reduction is anticipated because of increased burnup and increased power generation capability of PuC-UC, compared to presently available metallic fuels. The effect of high burnup and high power generation rate on the stability of PuC-UC is not known. However, based on UC irradiation tests, there is justifiable optimism that carbide fuels will be dimensionally more stable than metallic fuels. As a result of high melting point and good thermal conductivity of UC, there is further expectation that carbide fuels will be capable of high power generation rates.

The Carbide Fuel Development Program is concerned with the technology of the entire PuC-UC fuel cycle. The major goal of the program is to produce PuC-UC and to obtain data on its irradiation behavior for long burnups and at high power generation rates. In addition, other areas of the fuel cycle are being explored to discover potential problems. The program was initiated in May 1959 and as outlined covers a period of about four and one-half years. The program has the objectives as outlined below:

Conceptual Design

1. An analytical study of the effect of substitution of PuC-UC on heat transfer, physics, and cost of existing fast breeder reactors.
2. Conceptual design of rod-type, fuel element configurations which can be substituted directly in existing reactors.

The above was completed and was reported in NDA 2140-2.

Facility Design and Fabrication

1. Design and construction of a facility for carbide fabrication at The Carborundum Company.
2. Design and construction of a facility for carbide evaluation at NDA.

The above was completed and was reported in NDA 2145-6.

Fuel Fabrication and Evaluation

1. Explore various methods of fuel preparation and fabrication into cylindrical pellets, beginning with powders.
2. Evaluate pellets by density measurement, chemical analysis, x-ray diffraction, hardness, metallography, and fuel-cladding compatibility studies. This is essentially complete for UC.

Fuel Irradiation

1. Irradiate clad fuel samples with burnup and maximum fuel temperature as the major variables. A minimum 2% burnup and a minimum 650 ℃(1200 ℉) fuel temperature were selected to establish the economic advantages of the fuel.
2. Make a post-irradiation examination.

Fuel Reprocessing

Study the reprocessing of irradiated fuel.

Full Scale Fuel Assembly

Design and construct a full scale fuel element assembly for irradiation in an existing fast breeder reactor.

2. SUMMARY

2.1 FUEL FABRICATION AND EVALUATION

Nearly stoichiometric, low nitrogen content UC was synthesized in the plutonium glove box atmosphere. PuC and PuC-UC preparation studies were initiated by the oxide-carbon reaction.

UC with nickel additions lowered required sintering temperatures, improved density over control straight UC samples, but did not improve densities over those obtained previously with straight UC.

Microprobe analysis of niobium and $2\frac{1}{4}$ Cr-1 Mo compatibility samples tested 4,000 hr at 820°C, showed no uranium penetration.

2.2 IRRADIATION TEST

The W1-1 capsule containing two clad UC specimens continued operation to 11,000 MW-d/tonne by the end of April. The W1-2 capsule was inserted in WTR, but had to be removed after a short time because of a radioactive gas leak.

2.3 PLUTONIUM FACILITIES

2.3.1 Facility at The Carborundum Company

The facility started operation with plutonium in March. Modifications and maintenance continue to be required and are being completed with minimum effect on experimental work schedules.

2.3.2 Facility at NDA

The major modifications, the once-through nitrogen and helium systems, have been completed and initial operation has been satisfactory. A performance test was initiated prior to operations with plutonium. Design and construction of equipment for the furnace box are in progress.

3. FUEL FABRICATION AND EVALUATION

3.1 INTRODUCTION

The goal of the fabrication studies is to produce a high density combination of stoichiometric PuC and UC by powder fabrication techniques. A high physical density (about 95% of theoretical) is desired to minimize fission gas release and give a high fuel density.

The goal of the evaluation tests is to identify the material by density measurement, chemical analysis, x-ray diffraction and metallography. Additional out-of-pile tests of fuel-cladding compatibility, thermal stability, and coefficient of expansion will survey properties of interest for in-pile tests.

Studies with plutonium started during the quarter.

3.2 CARBIDE POWDER PREPARATION

During the initial part of this quarter the plutonium facilities operation methods and equipment were checked by experimental work with uranium carbide. Several sets of synthesis experiments were made. Each set consisted of three UO_2-carbon mixtures based on the assumption of O/U ratios of 2.00, 2.08, and 2.16. The mixtures were held at 1750°C for 2 hr. Samples from the initial experiments all had nitrogen contents in excess of 0.4 w/o, indicating high nitrogen content of the helium sintering atmosphere. Through the use of a new gas analyzer (see Section 5.2) capable of indicating qualitative nitrogen content in the helium, the nitrogen content of samples was reduced to less than 0.05 w/o in subsequent experiments. The results of the carbon analyses, while not entirely consistent, showed that essentially stoichiometric UC was obtained when the O/U ratio was assumed to be 2.00. The carbon contents were slightly high: 4.84 to 5.34 w/o.

Some experiments were carried out to determine if storage conditions of the reactants affected the product. The results are not conclusive, but there appears to be a tendency to lower carbon in uranium carbide made from reactants stored and batched in air rather than in the helium glove box. Carbon contents were in the 4.76 to 4.93 w/o range.

Synthesis experiments for the preparation of plutonium monocarbide were initiated in the middle of this quarter. Reaction batches of stoichiometric mixtures of plutonium dioxide and carbon were furnaced at temperatures ranging from 1300 to 1650°C with hold times of 2 hr in some experiments and 5 hr in others. PuO_2 used was prepared by oxidation of the metal by the Dow Chemical Co. A commercial carbon produced by cracking natural gas was used. Analytical results presently available appear in Table 1. None of the reaction products contained statisfactory stoichiometric material.

In all experiments except No. 5, the reacted material was visually at least two-phase. At temperatures of 1600°C and higher there were signs of melting and possible volatilization as evidenced by deposition of unknown material on the furnace exhaust filters.

Table 1 — Experiments on the Synthesis of PuC From PuO_2 and Carbon*
(Stoichiometric carbon content for PuC = 4.78 w/o C; however, PuC exists in the 45-47 a/o C range making the desired C content 3.95-4.26 w/o)

Experiment No.	Reaction Temp, °C	Hold Time, hr	Analysis of Product, % Pu	C	Pu+C	Comments
1	1350	2		10.17		
2	1425	5	89.85	6.55	96.40	Analysis of shell
			84.41	8.87	93.28	Analysis of core
3	1500	2	91.90	6.02	97.92	Analysis of shell
			86.34	8.08	95.42	Analysis of core
4	1500	5	92.64	5.79	98.43	Small core†‡
5	1550	5	93.26	5.91	99.17	Homogeneous throughout‡
6	1600	2	92.07	6.19	98.26	Not homogeneous, some fused spots‡
7	1650	2	93.42	5.71	99.13	Analysis of shell
			86.61	12.62	99.23	Analysis of core; evidence of incongruent melting.

*Mixtures were made in ratio of 1 part PuO_2 to 3 parts carbon.
†X-ray results by the camera method reveal Pu_2C_3 and PuO.
‡Chemical analysis represents the entire pellet.

One experiment was conducted on synthesizing a UC-PuC solid solution in the ratio of 4:1, respectively, by the carbon reduction of the mixed oxides. The reaction mixture was heated to 1550°C with a hold time of 5 hr. Chemical analysis on the product gave total carbon at 5.11%. The stoichiometric carbon content of the mix theoretically is 4.8 w/o C.

One synthesis experiment to prepare Pu_2C_3 was made. A stoichiometric mixture of plutonium dioxide and carbon was furnaced at 1550°C with a hold time of 5 hr. Chemical analysis on the product gave total carbon at 7.11% and plutonium at 92.87%. The stoichiometric carbon content of Pu_2C_3 is 7.0 w/o C.

3.3 CARBIDE PELLET FABRICATION

Additional experiments were made to determine if nickel would act as a densification aid in the sintering of UC. Straight UC pellets were carried along for purposes of comparison.

Pellets of UC and UC containing 1 w/o of freshly reduced nickel powder were pressed by cold forming at 20,000 lb/in.^{2}. In this experiment, the size of the pellet was 0.6 in. in diameter by about 0.25 in. long. The temporary binder was ½% Carbowax 6000.

The UC and UC-Ni pellets were sintered at 1450°C, 1600°C, and 1800°C with hold times of 4 hr. The atmosphere was helium at about atmospheric pressure. Results are shown in Table 2.

Table 2 — Results of Sintering UC with Nickel Additions

	Density (g/cc) after Sintering at Indicated Temperatures				
	As Pressed	1350°C	1450°C	1600°C	1800°C
UC + 1 w/o Ni	8.5	10.2	12.2	12.7	12.7
UC	8.5	8.5	8.5	10.2	11.0

The nickel sintering aid reduced required sintering temperature by several hundred degrees (C) and produced improved densities over the control UC samples. The UC-Ni densities, however, were comparable to those previously obtained with straight UC samples. Metallographic examination of samples is in progress.

3.4 FUEL-CLAD COMPATIBILITY TESTS

In order to study possible fuel-clad interactions under conditions similar to those which would prevail in an actual fuel element, a series of diffusion couples were tested. The carbide fuel was held in contact with various cladding materials at 820°C in a helium atmosphere. Following this, the couples were sectioned and the carbide-cladding interface examined by metallographic means, x-ray diffraction and microprobe analysis. Examination of the test specimens was completed during this quarter.

Microprobe analysis of the niobium and 2¼ Cr-1 Mo specimens indicated no uranium penetration. The specimens had been tested for 4000 hr. The nonmetallic phase on the surface of 2¼ Cr-1 Mo photomicrograph (Fig. 3.17, NDA 2145-6) had a high uranium content. The material is probably oxidized UC, which adhered to the surface of the steel.

3.5 ANALYTICAL METHODS

The carbon analysis method using titration as the final step was installed at the NDA Plutonium Facility. Carbon recoveries using SiC standards were improved by changing the design of the absorber tubes and changing the absorbing solution from NaOH to KOH. The UC_2 "standards" will be analyzed by this method.

The modified carbon analyzer at The Carborundum Co. was tested with the UC_2 "standards." The calculated precision was ±0.59% relative, at the 95% confidence level (two sigma).

The previously reported mounting method for x-ray powder camera samples was modified for safety reasons. The glass capillary used in the method described in previous reports was changed to a tungsten wire, coated with sample powder and a binder, enclosed in a gelatin capsule. Two sample mounts were made this way on materials resulting from plutonium carbide synthesis attempts. In the first case, Duco cement was used as the binder and after x-ray exposure, the physical characteristics of the sample changed considerably, from a coating on a wire to a globule at the end of the wire. No discernible patterns were detected on the developed film.

In the second case, collodion was used as the binder. After x-ray exposure, the only visible change noted was that the sample coating had apparently fluidized to a small extent; however, two distinct patterns, Pu_2C_3 and PuO, were detected on the developed film. (See Section 3.2.) The above work continues.

The plutonium analytical results reported in the Fabrication Section were based on a gravimetric method which assumed conversion of plutonium compounds to stoichiometric plutonium dioxide at approximately 800°C in an oxygen atmosphere. The above assumption has unknown validity at this time; however, the precision of the method appears to be good as based on the agreement of duplicates. Other plutonium analytical methods under consideration involve the dissolution of the plutonium compounds, including any and all oxides. Initial attempts (including acid fusion in $KHSO_4$) at dissolving the plutonium dioxide as received at Carborundum have been unsuccessful. The above work continues.

4. IRRADIATION TESTS

4.1 INTRODUCTION

In order for PuC-UC fuel to reduce fuel cycle cost, several conditions must be met. The fuel has to be able to achieve high burnup, high operating temperatures, and high power. At least 2 a/o burnup is desirable at fuel temperatures above 1200°F with maximum dimensional stability of the fuel and minimum release of fission products. Power density should be at least equivalent to presently planned fuels. The objective of the irradiation program is to determine whether the high burnup temperature and power density required can be achieved.

The irradiation test will measure temperatures, burnup, power density, and dimensional stability of the fuel.

4.2 IRRADIATION TEST

The current irradiation program is testing clad UC rods, each having a 0.191 in. diameter by 3 in. long fueled section. The space between the UC and cladding is filled with helium. The W1-1 capsule contains a niobium and a stainless steel clad specimen. The W1-2 capsule contains one stainless steel clad specimen. A detailed description of the capsules and specimens is given in NDA 2145-6, pp. 32-40.

The W1-1 capsule was started up in WTR on December 21. Burnup as of the beginning of May was about 11,000 MW-d/tonne. In order to obtain the desired 17,000 MW-d/tonne burnup the capsule will be removed in July rather than May. The longer irradiation time is necessitated by unscheduled reactor shutdowns and lower than anticipated flux at the specimen. Allowing a month cooling period, the hot lab examination will start in August. The specimen operating conditions are given in Table 3. The range of central temperatures has been 1190 to 1765°F (643 to 963°C) and the range of clad surface temperatures has been 700 to 890°F (371 to 477°C). The wide ranges of variation are due to variations in reactor power. In general the temperatures are lower than the planned 1800°F (980°C) central fuel and 1000°F (538°C) clad surface temperature. The reasons for this could be: lower reactor flux than estimated, greater flux depression by the experiment than estimated, and better specimen thermal conductivity than estimated.

A drop in the UC + He gap conductivity with burnup was reported in the previous progress report, NDA 2162-1. The conductivity returned to its startup value at about 6,000 MW-d/tonne. The power generation rate also increased at this time. (The reason for the increase is not known.) After 6000 MW-d/tonne the central thermocouple in the niobium clad specimen started to fail. Failure was first evidenced by continuous drop in central temperature with concurrent increase in the power generation rate. Complete failure occurred in May. The UC + He gap conductivity and He gap conductances at subsequent burnups can no longer be considered reliable. Table 4 shows the calculated gap conductances assuming reasonable conductivities for UC. The in-pile thermal conductivity of UC and the He gap conductance are interdependent. The value for one will depend on the assumptions made for the other.

Table 3 — Operating Data on W1-1 Specimens

	Central Fuel Temp, °F		Clad Surface Temp, °F		Heat Generation, w/in.		$\int_{ts}^{tc} Kd\theta$, w/cm		Avg Thermal Conductivity of UC + He gap, Btu/hr-ft^2-ft-°F	
Burnup MW-d/tonne	6,000	11,000	6,000	11,000	6,000	11,000	6,000	11,000	6,000	11,000
Nb Clad UC Sample	1310	1275†	810	740	770	780	24	25	5.3	5.3†
SS Clad UC Sample	1500*	1300†	880	720	795	715	25	22	5.3*	5.3†

*Estimate based on UC + He gap conductivity in the Nb clad specimen.
Prior to failure of the SS clad specimen central thermocouple, the UC + He gap conductivities measured in the two specimens were similar.

†Based on UC + He gap conductivity measured on Nb specimen at 6000 MW-d/tonne. The Nb specimen central thermocouple failed between 6000 and 11,000 MW-d/tonne.

Table 4 — Fuel and He Gap Conductivities

UC Thermal Conductivity Btu/hr-ft^2-ft-°F (Assumed)	He Gap Conductance of Nb Clad Specimen,* Btu/hr-ft^2-°F at 6,000 MW-d/tonne
10	2830
12	2375
14	2110

*Measurements after initial startup indicated the gap conductances of the Nb and SS clad specimens to be similar.

The W1-2 capsule was inserted in WTR during the February shutdown. After three days of operation, fission product activity was detected in the pressure probe line. The capsule was cut out of the reactor and removed to the hot cell. The pressure probe was leak-tested and found to leak through the probe body. The probe will be sectioned to determine the cause of failure.

A review of the performances of the W1-1 and W1-2 capsules is being completed to determine their suitability for the PuC-UC irradiations.

5. PLUTONIUM FACILITIES

5.1 INTRODUCTION

The Carborundum Company has constructed a facility to be used for fabricating the fuel. NDA has constructed a facility to be used for fuel evaluation and irradiation specimen preparation, and will construct facilities for post-irradiation examination and "hot" reprocessing.

5.2 FACILITY FOR FUEL CARBIDE FABRICATION AT THE CARBORUNDUM COMPANY

Continued satisfactory operation of the plutonium facility permitted initiation of work with plutonium during March. Modifications to and maintenance of the facility continue with a minimum effect on the plutonium experimental work schedule.

The following modifications were completed during this quarter.

1. The replacement helium pump was received, installed, and is operating satisfactorily.
2. A new and improved cold cathode ionization detection type of gas analyzer was fabricated and installed in the helium system. The analyzer appears to have good sensitivity to nitrogen contamination as measured by the change in color of the glow discharge.
3. Additional helium system modifications were a direct gas fill system for the helium pump tanks, an automatic high pressure bleed-off for the helium recirculating system, a check valve on the helium inlet manifold, larger area filters on the static pressure lines, replaceable filter on the furnace exhaust line.
4. An emergency compressed air supply and additional electric power were installed.
5. An alpha counting area was established on the hot side of the clothes change room.
6. An alarm for box exhaust fan failure was tied into the existing ADT alarm system.

Work in progress includes the automatic changeover system for the helium pumps, build up of a spare parts inventory, and completion of an operating manual.

Maintenance was required for several valves. In some cases this required breaking into the piping system. Comtamination was encountered in two of the instances, indicating that plutomium had leaked past the absolute box filters. Whether the leakage is through or around the filters is not known. The problem is being investigated. A bad exhaust fan bearing required replacement. The preheaters of the getter furnaces burned out and are being replaced.

5.3 FACILITY FOR FUEL CARBIDE EVALUATION AT NDA

The required modifications to the plutonium facility were completed during this quarter. A performance test specification was written and the performance test was initiated to demonstrate the satisfactory operation and safety of the facility. The performance test consists of three phases:

1. facility checkout (24 hr) – start up of the gas systems and facility instrumentation to provide proper operating conditions;
2. acceptance test (6 days) – continued operation of the facility, without experimental operations in the boxes, to demonstrate proper pressure controls, impurity controls, and flow rates in the facility;
3. normal operating test (4 weeks) – continued operation of the facility to demonstrate proper pressure controls, impurity controls, and flow rates in the facility, while doing experimental work, transfer operations, glove changes, waste removal, and contamination control using uranium.

Operations with plutonium will commence upon satisfactory completion of the performance test.

Prior to the performance test a number of tests and modifications were made in the facility. The piping of the once-through nitrogen system was simplified considerably. The nitrogen and helium gas headers were modified. The nitrogen and helium piping and box systems were leak-checked and found helium leak-tight. The nitrogen line was purged and was able to maintain 400 ppm oxygen at operating flow rates. The maximum desired level is 500 ppm oxygen. The helium box was purged and was able to maintain 20 to 60 ppm oxygen at operating flow rates. The maximum desired level is 100 ppm oxygen. The following modifications were completed during this quarter.

1. Pressure control was modified to provide stable operation during normal and emergency conditions. Additional pressure regulators were installed and the proper pressure pickup points were determined.
2. Manometers were installed, in addition to Magnahelic gages.
3. The gas analyzer was adapted for oxygen analysis in both nitrogen and helium. A filter was installed in the sampling line.
4. A dewpoint meter was installed in the gas sampling line.
5. The requirements for making a helium leak-tight 16 in. port seat were determined.
6. A method was developed for attaching helium leak-tight, thin aluminum sheet covers and tunnels over large plastic sheet areas that are prone to moisture diffusion. The sheet forms are attached by a special adhesive and can be cut from the system easily.

Items in progress include: a check valve near the exhaust blowers to prevent excessive vacuum in the boxes, a shutoff valve for the helium box vacuum system to prevent excessive vacuum in this box, a duplicate alarm panel, improved clamps for O-rings on box ports, a spare parts list, and an operating manual. Considerable maintenance has been required for the oxygen analyzer. The possibility of buying a different unit is being considered.

The design and construction of the equipment for the furnace box is in progress. A silicon-carbide resistance element furnace will be used for the vacuum or inert gas atmosphere dilatometer. The dilatometer will have alumina elements in an alumina protection tube. Temperature limitation will depend on the ability of available alumina tubes to hold an atmosphere. The expected maximum range is 1500° to 1800°C. The core of the furnace has been constructed and test runs are being made. The majority of the components for the dilatometer have been ordered and some received. A tantalum resistance furnace (2500°C max.) was chosen to study melting points and thermal stability. An order for a commercial unit (R. D. Brew and Co.) was placed. Design of the adaption of the unit to the glove box is nearly complete.

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