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AN INFORMAL REPORT

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Quarterly Status Report on the

Advanced Plutonium Fuels Program

July 1 through September 30, 1971

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

UNITED STATES
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This LA. . .MS report presents the status of the LASL Advanced Plutonium Fuels Program. The four most recent Quarterly Status Reports in this series, all unclassified, are:

LA-4546-MS	LA-4693-MS
LA-4595-MS	LA-4749-MS

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An Informal Report
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FAST REACTOR REPORT
SPECIAL DISTRIBUTION
ISSUED: October 1971

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Advanced Plutonium Fuels Program

July 1 through September 30, 1971

compiled by

R. D. Baker

FOREWORD

This is the 21st quarterly report on the Advanced Plutonium Fuels Program at the Los Alamos Scientific Laboratory.

Most of the investigations discussed here are of the continuing type. Results and conclusions described may therefore be changed or augmented as the work continues. Published reference to results cited in this report should not be made without obtaining explicit permission to do so from the person in charge of the work.

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PROJECT 401

EXAMINATION OF FAST REACTOR FUELS

Person in Charge: R. D. Baker
Principal Investigators: J. W. Schulte
K. A. Johnson
G. R. Waterbury

I. INTRODUCTION

This project is directed toward the examination and comparison of the effects of neutron irradiation on LMFBR Program fuel materials. Unirradiated and irradiated materials will be examined as requested by the Fuels and Materials Branch of DRDT. Capabilities are established and are being expanded for providing conventional preirradiation and postirradiation examinations. Nondestructive tests will be conducted in a hot cell facility specifically modified for examining irradiated prototype fuel pins at a rate commensurate with schedules established by DRDT.

Characterization of unirradiated and irradiated fuels by analytical chemistry methods will continue, and additional methods will be modified and mechanized for hot cell application. Macro- and micro-examinations will be made on fuel and cladding using the shielded electron microprobe, emission spectrograph, radiochemistry, gamma scanner, mass spectrometers, and other analytical facilities. New capabilities will be developed in: gamma scanning, analyses to assess spatial distributions of fuel and fission products, mass spectrometric measurements of burnup and fission gas constituents, chemical analyses, and measurement of carbon in irradiated fuels.

Microstructural analyses of unirradiated and irradiated materials will continue using optical and electron microscopy, and autoradiographic and x-ray techniques. Special emphasis will be placed on numerical representation of microstructures and its relationship to fabrication and irradiation parameters. New etching and mounting techniques will be developed for high burnup materials.

II. EQUIPMENT DEVELOPMENT

A. Inert Atmosphere Systems

(P. A. Mason, R. F. Velkinburg)

1. Disassembly Cell

The atmosphere was maintained continuously during the report period by the recirculating purifier. Manipulator boots were replaced on August 23 because of a high leak rate. Typical purity levels of 5 to 10 ppm O_2 and < 5 ppm H_2O were maintained except for a short period in early August when it was not possible to regenerate the purifiers on a regular schedule. A maximum level of 1700 ppm O_2 and 270 ppm H_2O is believed to have been reached during this period. Leakage at the transfer port for the alpha seal tubes resulted in typical readings of 35 ppm O_2 and 8 ppm H_2O during most of the week of September 12, until the alpha tube was removed and the cap assembly replaced.

2. Metallography Cells

During July the atmosphere purity was being maintained satisfactorily with the recirculating purifier. Typical readings of 3.5 to 5 ppm O_2 and < 5 ppm H_2O were recorded. Oxygen and moisture concentrations increased sometime during the week of August 2, with typical readings of 100 to 250 ppm O_2 and 20 to 25 ppm H_2O being maintained since that time. During the night

of September 15, a very large increase in oxygen level resulted in severe overheating of the catalyst pellets. Temperatures reached a level sufficient to partially melt silver-soldered seams near the bottom of the tanks. The catalyst pellets were partially fused together resulting in an increased pressure drop across the KBM catalyst tank which overloaded the recirculating pump drive motor and tripped the power breaker. The polishing box was automatically switched to an Ar purge of 40 cfh through the Model "L" manipulator boots. (This system was described in the October-December 1970 Quarterly Report LA-4595-MS). With the recirculating system isolation valves open between the two cells, the cells reached a maximum reading of only 300 ppm O_2 recorded by the oxygen analyzer, even though high concentrations of O_2 reached the catalyst unit.

The only identified air leak in the system is at the seal between a Model "L" manipulator adapter sleeve and an alpha box port in the polishing cell, but this had been present for a week prior to the incident. All efforts to locate a significant leak source outside the shielded cell enclosure, including the purifier system, were unsuccessful. During the period since the incident, rapid and significant changes in the leak rate of both cells have occurred during and outside working hours.

3. Hardware Development

Design modifications are in progress on the CRL Model "L" manipulator adapter sleeves to correct the difficulty which had been experienced in obtaining an adequate seal to the alpha box manipulator ports with the two original units.

B. Sealed Manipulators

(P. A. Mason, C. D. Montgomery, R. F. Velkinburg)

Three additional pairs of sealed Model "L" manipulators were received. These units will be installed in an inert atmosphere containment boxes (as time permits) to assure a high purity atmosphere and to minimize the flow of argon used in purging the boots.

Complete check-out and testing of these manipulators is currently in progress. Several improvements are being made to the LASL-furnished wall adapter tubes.

C. Shipping Casks

(C. D. Montgomery, J. W. Schulte)

A duplicate of cask DOT SP-5885 having a capacity for shipping fifteen 40-in-long fuel capsules will be delivered in October 1971. It is expected that the small cask, suitable for shipping short sections of pins, will be available for use in November.

An electro-mechanical elevator has been designed and fabricated and is being assembled for use with the Rover casks. This device can be actuated remotely to raise or lower various cask inserts for facilitating loading and unloading operations.

D. New Metallograph Blister

(K. A. Johnson, C. D. Montgomery, J. M. Ledbetter, J. L. Lehmann, T. Romanik, R. F. Velkinburg)

Work has continued on assembling the shielding compartments for the new metallograph chamber which will house both the Bausch and Lomb and the new Leitz units.

Modifications to the containment box and shielding have been made to accommodate:

1. The mercury vapor light and seal assembly.
2. A bag-out port for removal of films from alpha and beta-gamma autoradiography. Small items having a low beta-gamma level may also be removed from this port.
3. An improved adapter to provide easier installation and removal of the conveyor system between the polishing box and the metallograph blister.
4. Additional roller support assembly for the Leitz Metallograph.

The assembly and check-out are nearly complete. The box and modular shield components will be sandblasted prior to painting.

E. New Mechanical Profilometer

(M. E. Lazarus, C. D. Montgomery, T. Romanik)

The initial drafting layout has been completed on the new mechanical profilometer. The new unit will have a more sturdy frame and a much more easily replaced LVDT than the present unit. Fuel element loading and unloading will also be facilitated.

It is planned that this unit, which will replace the profilometer currently located in the Disassembly Cell,

will be used as a back-up for the Optical Profilometer and also be available for use on breached pins.

F. Butyl Acetate Removal System
(G. S. Dow, M. E. Lazarus)

A refrigeration unit for removing butyl acetate (used as a grinding vehicle and in the ultrasonic cleaners) from the recirculating inert gas streams is being designed. The unit which will be incorporated into the Ar Purification System is ready to be ordered.

G. High Pressure Metallographic Sample Potting System
(C. D. Montgomery, T. Romanik, D. S. Shaffer)

A high pressure potting system (4000 psi) is being designed for ultimate use in the shielded containment boxes. The prototype system will be hydrostatically tested before cold runs are made.

This technique is shown to provide higher quality specimens and to minimize the need for repeated impregnation of porous materials.

H. Scanning Electron Microscope
(K. A. Johnson)

PuO_2 and UO_2 powders were examined this Quarter. Alpha-fixing and containment procedures were developed which made possible examination of these materials.

The shielded transport and specimen holders for irradiated samples are being fabricated.

I. Other Microstructural Analysis Equipment and Developments
(R. Beckman, K. A. Johnson, K. L. Walters)

1. A prototype high pressure impregnation system has been designed for use in a glove box. Component procurement and fabrication are in process.

2. A computer code IMAGE III has been written for improved data manipulation and interpretation. A plotting subroutine is now being developed.

3. A theoretical study has been initiated on the statistics of pore size distribution based on pores of random shape with respect to measurements which can be made on a two dimension sample.

4. A new stage with electric drive has been ordered for the existing Bausch and Lomb remotized metallograph.

5. The prototype ion etcher is being fabricated.

III. HOT CELL FACILITY AT DP WEST
(F. J. Fitzgibbon, M. E. Lazarus, J. M. Ledbetter, C. D. Montgomery, J. R. Phillips, J. R. Trujillo, R. F. Velkinburg)

It is planned to complete most of the installation and testing of equipment for the nondestructive examinations in the DP West Hot Cells during the Second Quarter of FY 1972. Additional delays were caused during the First Quarter by a lengthy strike and a prevalence of other urgent tasks.

A. Structures and Building Equipment

Enclosing and air conditioning of the balcony area remain to be completed. This area will house the data processing equipment for gamma scanning and profilometry.

Approximately 100 h of electrical work remain to be done in connecting the radiation monitors, mercury vapor lights, hoist controls, and other ancillary equipment.

B. Hot Cell Equipment

1. Gamma Scanning Equipment

It is planned to maintain the present gamma scanning facility until the new system is completed and satisfactorily tested.

Some sections of the collimators have been completed. However, the precision holes which are provided by a special technique are yet to be finished.

2. Electro-Optical Profilometer

The new light source has been received, tested, and installed at DP West. It still does not meet the exact specifications promised but is suitable for use. The remaining equipment has been installed with the exception of the high speed data storage system. In-cell testing disclosed that a few changes could be made to aid the cell operator in loading and unloading the equipment. One change was to motorize the centering roller diameter adjustment as shown in Fig. 401-1; another change was the incorporation of a push-pull cable to allow remote fuel element clamping. Before measurements can be made on irradiated pins, shielding must be provided where the periscope through-tube extends into the operating area.

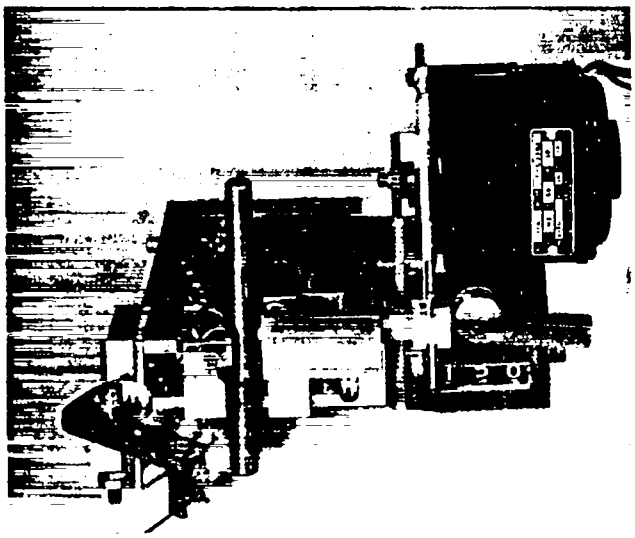

Fig. 401-1 Fuel Element Centering Fixture for Optical Profilometer

A high precision standard with tolerances to ± 30 micro-in. was prepared for checking linearity of the profilometer. The profilometer linearity is within ± 100 micro-in. over a 20 mil field of view. A Dumont Model 440 Oscilloscope will aid in aligning the profilometer system.

3. Pulsed Eddy Current Scanner

A Pulsed Eddy Current Scanner will be installed at DP West. Design of the scanner assembly is now underway. Group GMX-1 will supply the sensors and electronics.

IV. METHODS OF ANALYSIS

A. Measurement of U and Pu
(J. W. Dahlby)

1. By Coulometric Titration

Controlled-potential coulometry has been used successfully to measure U and Pu without chemical separation in solutions of mixed oxides and mixed carbides having undergone as much as 6 at% burnup. The Pu is measured by integrating the current for the coulometric oxidation of Pu(III) to (IV) at a Pt electrode, then integrating the current for the coulometric reduction of Pu(IV) to (III), and averaging the results. The U content is obtained from the integrated current for the coulometric reduction of U(VI) to U(IV) at a Hg electrode, following a preliminary reduction of more easily reduced impurities.[1] The precisions (1σ) of the methods were 0.3% for the U titration and 0.1% for the Pu titration. These methods were less precise, however, when applied directly to measurement of U and Pu in fuels having undergone 8 at% burnup, presumably because of the greater amounts of radiolytic products caused by the intense radioactivity. For this reason, the methods were modified to include separation of fluoride-insoluble fission product elements to reduce the $\beta - \gamma$ radiations prior to the coulometric titrations. In the separation tried, the U and Pu were oxidized with Ag(II) to their fluoride-soluble (VI) oxidation states while a scavenging precipitation was made using La as the carrier and HF as the precipitating agent. Preliminary tests showed that this separation lowered the $\beta - \gamma$ radioactivity level by a factor of ten.

The modified methods were tested by analyzing aliquots of a solution having known concentrations of unirradiated U and Pu as a stand-in for irradiated fuel. Titrations of the U and Pu in 8 aliquots of this solution, following the scavanging precipitation of LaF_3, showed an average of 99.8% of the U was recovered but the apparent recovery of Pu was slightly high, 100.5%. It was found that a positive bias was caused by deposition of Ag during the coulometric titration of Pu. Precipitation of Ag as AgCl prior to the titration eliminated the interference, and the Pu recovery was reduced to 100.0%. Analyses of the fluoride precipitates showed that they contained no more than 25 μg of Pu which was approximately 0.02% of the amount in the original sample.

As this modified method with the fluoride precipitation seems satisfactory, further tests are being made by determining U and Pu in $(U,Pu)O_2$ fuels having undergone 8 at% burnup or more.

2. By X-Ray Fluorescence
(J. M. Hansel, E. A. Hakkila)

A rapid, non-destructive identification of fuel and insulator pellets, and a measurement of U and Pu contents, would aid substantially in quality control evaluations of pellets and in locating various types of pellets in a fuel stack during pin loadings or examination. X-ray fluorescence spectrometry is being evaluated for this purpose. In the proposed technique, the intensities of the L_{α_1} x-rays for U and Pu from the whole pellet are

measured, and the absolute intensities or the ratio of the intensities of the U x-ray and the Pu x-ray are used to determine the U and Pu weight fractions. The whole pellet is positioned precisely in a special copper slug holder in the sample compartment of the x-ray spectrograph. The face of the pellet is excited using a W-target x-ray tube operated at 50kV and 40 mA, and the characteristic x-rays are counted while the sample is rotated rapidly.

To test this measuring technique, the U and Pu x-ray intensities were measured three times from each end of four $(U,Pu)O_2$ pellets from the same batch of fuel. The relative standard deviations were 0.74% in measuring U and 1.0% in measuring Pu. These precisions are about equal to the relative standard deviation of 0.8% for fourteen measurements of each element in one fuel pellet. These data show that the pellets can be positioned reproducibly in the holder. The relative standard deviation for measuring the U/Pu x-ray intensity ratio was 1.3%, but this measurement was less sensitive to faulty positioning of the pellet. This investigation is continuing to determine which method of calculation is preferable and to evaluate other factors including fuel density. Pellets having homogeneous and accurately known U and Pu contents would be needed for calibrating the method.

B. Determination of Carbon and Hydrogen
(T. K. Marshall)

Investigations of the effects of C and H on fuel-cladding interactions and other phenomena occurring during irradiation of reactor fuels require reliable measurements of these elements in various cladding materials and in oxide and carbide fuels. One well-tested determination of C and H consists of burning the sample in pure O_2 gas at 1000°C to convert these elements to CO_2 and H_2O which are trapped and weighed. A combustion furnace and associated equipment for burning irradiated fuel and cladding samples were installed in a hot cell enclosure for this determination. The furnace consists of a fused-silica tube surrounded by a Kanthal-1 type resistance heater capable of heating the sample at least to 1000°C. The gaseous combustion products are swept by the O_2 gas flow through a CuO-$PbCrO_4$ mixture at 600°C to assure complete oxidation of CO to CO_2, and then through heated stainless steel tubing out the front wall of the hot cell and into $Mg(ClO_4)_2$ and Ascarite-filled absorption tubes to collect the H_2O and CO_2, respectively, for subsequent weighing. The carrier gas stream is returned into the cell for disposal. This measurement should be applicable to C and H concentrations ranging from 20 ppm to a few percent by weight.

Initial tests of the equipment showed that the apparatus blanks were low and consistent. Analyses of standard materials are now being made in preparation for further testing using irradiated fuel and cladding samples.

A LECO Low Carbon Analyzer also is being tested to provide an additional capability for measuring C. In this equipment, the sample is burned in O_2 at approximately 1700°C in an inductively heated furnace, and the CO_2 produced is measured in a simple gas chromatograph. Following calibration of the analyzer using commercial C standards, analyses of Standard Reference Material open hearth iron from the National Bureau of Standards showed that the apparatus function properly out-of-cell. Modifications to remotize the induction furnace section are planned prior to installation in a hot cell and further testing.

V. REQUESTS FROM DRDT

A. Examination of Unirradiated Fuels
(K. A. Johnson, E. D. Loughran, R. A. Morris, J. R. Phillips, J. W. Schulte, G. R. Waterbury)

Optical microscopy, electron microprobe and x-ray lattice parameter measurements have been made on representative samples of 20 mixed oxide fuels pellets from WARD. The final report is now being prepared.

B. Examination of Irradiated Material

General Electric Company: Samples of irradiated mixed oxide fuel specimens were received in June 1971 for the purpose of performing melting point determinations.

The samples were prepared and transferred to the DTA cell. Details of the examination are reported under Project 463, "Fuel Properties" section of this report.

Gulf United Nuclear Fuels Corporation: Eleven capsules, previously designated as UNC, were received on September 10 following irradiation in EBR-II.

Examinations made on Gulf United materials during this period are tabulated below.

TABLE 401-1

POSTIRRADIATION EXAMINATION OF GULF UNITED MATERIAL

	Examination	UNC Pin Identity
1.	Visual Inspection	102 through 112
2.	Measurements of Contamination and Radiation	102 through 112
3.	Measurement of Temperature	102 through 112
4.	Center Point Balance	102 through 112
5.	Micrometer Measurement	102, 103, 104, 106, 107
6.	Radiography	102 through 106
7.	Gamma Scanning	102 through 106
8.	Sectioning	92, 96, 99, 104
9.	Fission Gas Sampling[a]	107, 108

[a] No gas was available for analysis because of the ruptured condition of the pin cladding

Gamma scanning, to include three diametral and one axial gross gamma scans and some multispectral scans, was completed on UNC-138, -146, -187, -192, and -194. Detection of ^{137}Cs outside the fuel cladding on one of these pins showed that it had failed during irradiation. Reports on the analyses of UNC-138 and -146 were distributed.

Microstructural examinations of five specimens each from UNC-92, -96, -99, and -104 are in progress. The examinations, carried out in an argon atmosphere, are macrophotography, alpha and beta-gamma autoradiography, and optical microscopy (including mosaic preparation).

Cross sections from each of two fuel pins, UNC-126, and -219, were examined using the shielded electron microprobe.

Los Alamos Scientific Laboratory: Capsule 36-B was returned in July 1971 to EBR-II for re-insertion.

Nuclear Materials and Equipment Corporation: The examination program, agreed upon by representatives of ANL, LASL, and ORNL and approved by DRDT, was continued on the eleven pins received on November 25, 1970.

Microstructural examinations in an argon atmosphere consisting of macrophotography, alpha and beta-gamma autoradiography and optical microscopy (including as-polished and etched mosaics) were completed on: seven specimens from NUMEC pin A-10, 5 specimens from NUMEC pin A-11, and two specimens from NUMEC B-11.

Microprobe examination is in progress on a NUMEC A-11 fuel-cladding specimen. A cross section sample from section A of NUMEC A-10 was examined in detail using the shielded electron microprobe. Reaction layers in the cladding of two of the pins were found to contain significant concentrations of N_2, presumably from impurities in the fuel.

Oak Ridge National Laboratory: Work has started in preparing sections of fuel from NUMEC A-5, -8, -9, -10, and -11 for shipment to ORNL for Chemical Processing Studies. NUMEC A-6 will be sampled for fission gas and then sectioned; all sections of the pin will be shipped to ORNL.

Miscellaneous

Results of the examinations were forwarded to DRDT, the experimenter, and ANL for Safety Analysis (where appropriate) as various phases of the work were completed.

A meeting has been set up in October with DRDT, HEDL, and LASL representatives for the purpose of discussing the examination of some HEDL pins at the LASL facility.

Preliminary discussions have also been held regarding examination of several GE pins at LASL.

VI. REFERENCES

1. G. R. Waterbury, G. B. Nelson, K. S. Bergstresser, C. F. Metz, LA-4537, Los Alamos Scientific Laboratory (1970).

PROJECT 463

CERAMIC PLUTONIUM FUEL MATERIALS

Person in Charge: R. D. Baker
Principal Investigator: J. L. Green

I. INTRODUCTION

The primary objective of this program is the overall evaluation of the most promising of the candidate fuel systems for advanced LMFBR application. Emphasis currently is placed on the study of the relative merits of stainless steel clad nitride and carbide fuels under conditions that appropriately exploit the potential of these materials to operate to high burnup at high power densities. The major portion of the program is the evaluation of the irradiation performance of these fuel element systems. A continuing series of irradiation experiments is being carried out under steady state conditions in fast reactor environments to assess the effects of damage and burnup on stainless steel clad, sodium bonded, carbide and nitride fuel elements. These experiments are designed to investigate fuel swelling, interactions between the fuel and clad and thermal bonding medium, fission gas release, and the migration of fuel material and fission products as a function of burnup and irradiation conditions. In addition, experiments are being designed to allow the study of the effects of rapid, overpower, reactor transients on sodium bonded fuel assemblies. Continuous efforts are necessary in the development of fuel material preparation and fabrication procedures as well as the techniques required for the characterization of fuel materials both before and after irradiation.

A second objective in the program is the determination of thermophysical, mechanical and chemical properties and characteristics of plutonium-containing ceramics that are required for their evaluation and use as fuel materials. A broad range of capabilities in this area has been developed, including the study of (1) phase relationships using differential thermal analysis, (2) thermal transport, (3) thermal stability and compatibility, (4) hot hardness and its temperature dependence, (5) structure and phase relationships using high temperature x-ray and neutron diffraction, (6) thermal expansion, and (7) compressive creep rates as a function of temperature and stress. Several of these techniques are available for use with irradiated fuels.

II. IRRADIATION TESTING

The objective of the irradiation testing program is the overall evaluation of the most promising of the candidate fuel systems for advanced LMFBR application. The irradiation experiments are carried out under conditions that take advantage of the potential of these materials to operate to high burnup at high power densities.

A. Fuel Synthesis and Fabrication

(M. W. Shupe, K. W. R. Johnson, C. Baker, H. Moore, R. Walker, J. Reavis, and R. Honnell)

1. Carbide Production

Process development is being carried out to define conditions necessary for the production of carbide fuel required for the fabrication of the singly

encapsulated 19-pin subassembly. Specifically, techniques are being sought which will allow the production of sintered pellets having densities of 95 ± 2% T.D. (T.D. 13.43 g/cm^3). A simple approach to attaining this density is to reduce the particle size of the powder below that currently prepared. The effect of dry ball milling on particle size and powder purity is shown in Table 463-I. A significant reduction in the particle mass median diameter is obtained using all stainless steel equipment and a 16 hr milling period. Milling for an additional 16 hr results in further but smaller incremental size reduction. The particle size can also be reduced by additional oscillatory milling. The contamination of powders by Fe from stainless steel equipment varies over a moderate range. The W impurity levels are acceptably low for powders milled in all of the combinations of equipment materials investigated.

2. Equipment Development

Equipment to be used for the production of carbides under improved conditions is being designed and procured. A high temperature tungsten-mesh furnace is being installed in a new recirculating inert glove box. Orders for an additional high temperature furnace have been placed. Two new hydrogen treatment furnaces are being designed to permit increased production capacity and purer preparations. A recirculating inert box presently located in another Los Alamos site has been obtained and is being transferred to the DP Plutonium Facility. This unit will be used for powder processing of nitride fuel materials.

TABLE 463-I

EFFECTS OF COMMINUTION OF POWDERS

Lot No.	Milling Condition			Powder Size (mass median diameter, μm)		Impurity Increase (ppm)	
	Time (hr)	Jar	Balls	Initial	Reduction	Fe	W
118-1	16	S.S.	S.S.	6.5	2.7	165	—
118-2	16	S.S.	S.S.	6.6	2.3	80	—
118-3	16	S.S.	S.S.	6.4	1.3	95	—
126-3	32	S.S.	S.S.	5.5	0.9	—	—
128-3	16	WC	WC	—	—	—	35
2-2-2	24	WC	WC	—	—	—	10
128-4	16	S.S.	WC	—	—	30	25
130-3	16	S.S.	WC	—	—	75	10
144-1	1 hr oscillatory			4.2	1.5	—	—

3. Nitride Pellet Evaluation

The nitride fuel for the initial loading of the LASL carbide-nitride subassembly will be provided by Battelle Memorial Institute, Columbus. None of the fuel material has been received, to date, but a small number of chemically typical, solid solution, nitride fuel pellets have been received for preliminary evaluation. The following characterization steps have been carried out:

a. Visual inspection,
b. Dimension measurement, where possible,
c. Microstructural examination,
d. Pellet density measurement,
e. Sampling for analysis for major constituents and oxygen,
f. X-ray powder diffraction analysis,
g. Determination of the effect of heating on the microstructure of the pellets,
h. Sampling for the evaluation of U-Pu homogenity.

As soon as chemical analysis results are available, a summary evaluation will be reported. This material is atypical in that the pellets were rejects from a fabrication development experiment, and all were badly fragmented. For that reason, no radiographic examination for as-fabricated cracks will be carried out.

4. Process Development

Two procedures have been developed for the production of carbides meeting the necessary physical specifications and requirements for chemical and metallographic purity. The first is based on the direct combination of the elements by arc melting. This technique requires the availability of high purity uranium and plutonium metal as starting materials. High purity oxides of uranium and plutonium can be prepared considerably more cheaply than the metals; an economic advantage can be realized by utilization of a carbothermic reduction process using oxides as starting materials. The principal disadvantages of the carbothermic reduction process, as commonly applied, is the difficulty of producing single phase

material and the typically large oxygen contamination levels in the product. Developmental work is being carried out, as part of this program, to devise a carbothermic procedure that eliminates these disadvantages. A preliminary flowsheet of the LASL carbothermic oxide reduction process is shown in Fig. 463-1. In this process, the initial reduction is carried out using a small excess of carbon to guarantee the presence of higher carbides in the product. This is done to provide a driving force for the removal of oxygen. The reduction reaction is carried to completion by using appropriate temperature cycles in a high vacuum furnace. The higher carbides present in the reduction product are then removed by the application of the hydrogen reduction procedure which is in routine use at LASL. Properly applied, this process should produce a powder that is single phase monocarbide having a low oxygen contamination level.

Preliminary scoping experiments have been carried out using this procedure. Finely divided graphite, UO_2, and PuO_2 in appropriate proportions were mixed by ball milling. The form of the initial powders and the intimacy of the mixture are expected to be important process variables, so a scanning electron microscope is being used for qualative powder characterization. A typical heat treatment cycle is shown in Fig. 463-2. The chemical analyses of products from two trial reductions (before hydrogen reduction) are shown in Table 463-II. The oxygen concentrations in the products, particularly from run CBT-A, are sufficiently low to demonstrate the chemical feasibility of the process. Further development is in progress.

B. EBR-II Irradiation Testing

(J. O. Barner)

TABLE 463-II

CHEMICAL ANALYSIS OF CARBOTHERMICALLY PREPARED CARBIDES

Element	Gram-Atom/Mole Carbide CBT-A	Gram-Atom/Mole Carbide CBT-B	Concentration, wt% CBT-A	Concentration, wt% CBT-B
U	0.810	0.814	75.8	76.5
Pu	0.190	0.186	18.12	17.82
C	1.104	1.207	5.56	5.82
O	0.003	0.012	0.021	0.077

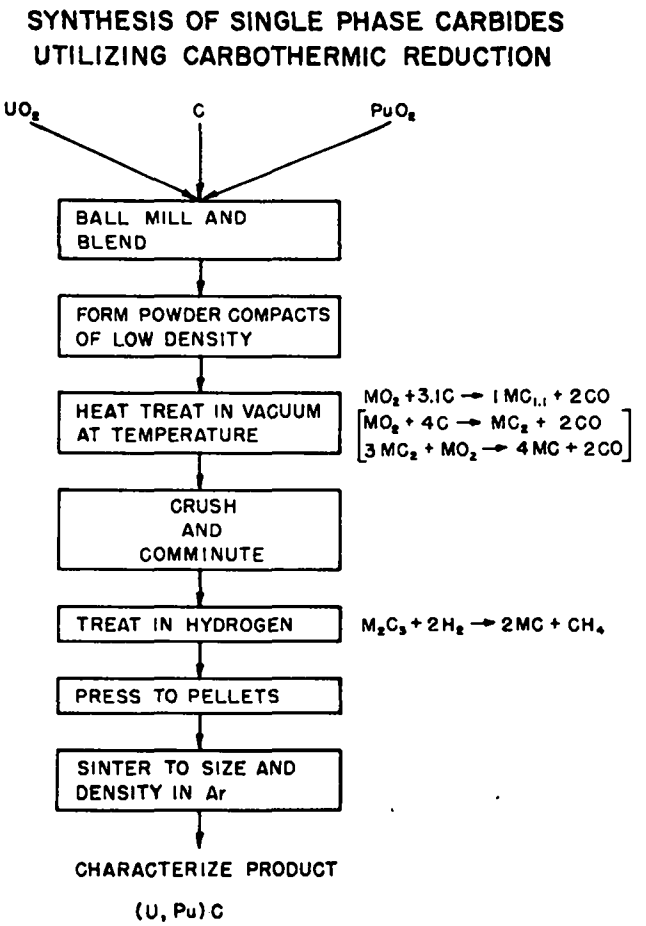

Fig. 463-1. Flow diagram for the LASL carbothermic reduction process for the preparation of high purity, single phase carbides.

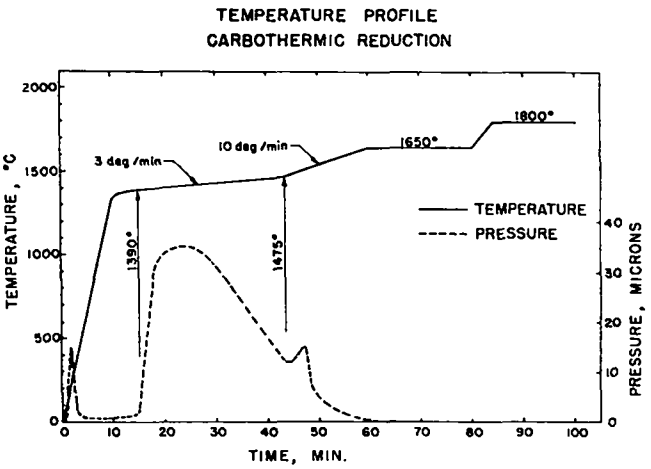

Fig. 463-2. Temperature and pressure profiles for the carbothermic reduction reaction.

The purpose of the EBR-II irradiations is the evaluation of candidate fuel/sodium/cladding systems for application in advanced LMFBR reactors. In the designs currently under investigation, fuel pellets of single-phase, solid-solution $(U_{0.8}Pu_{0.2})$ C or $(U_{0.8}Pu_{0.2})$ N are sodium bonded to Type 316 stainless steel claddings. Four series of experiments are planned. The three series for which approval-in-principle have been received from the AEC are described in Table 463-III. The fourth series is composed of nineteen singly clad fuel elements. Approximately one half of the elements will contain carbide fuel, while the remainder will contain nitride fuel.

One of the important purposes of this subassembly is to provide data to allow a critical comparison to be made of the overall irradiation behavior of carbide and nitride fuel pins which have been irradiated under conditions that are, as nearly as possible, identical.

The status of the Series -1, -2, and -3 experiments is summarized in Table 463-IV. EBR-II subassembly X119 was removed from the reactor near the end of the quarter and placed in the holding basket. This transfer was necessitated by the increased requirements for reactor reactivity which resulted from the insertion of several higher priority structural and control material experiments. It is expected that subassemblies X142 and X086 (after it is rebuilt following interim examination) will not be immediately inserted into EBR-II due to the same problem. EBR-II personnel indicate that these experiments will continue irradiation as soon as enough higher priority experiments have been completed to compensate for the loss of reactor reactivity.

The majority of the work during the quarter was devoted to the design of the nineteen element singly clad subassembly, pending approval-in-principle from AEC. The tentative experiment description is shown in Table 463-V. The experimental variables include fuel type, cladding cold-work, smear density, heating rate, operating temperature, and burnup. The carbide fuels will be 95% dense, single-phase $(U_{0.8}Pu_{0.2})$ C. The carbide fuel will be fabricated from material synthesized using both the arc-melting and carbothermic reduction processes. The nitride fuel for the initial loading will be supplied by Battelle Memorial Institute and will be prepared by the hydride-nitride process. The claddings will be 0.310 in. O.D. with 0.012 in. walls. The claddings for the tests

TABLE 463-III

Description of Series -1, -2, and -3 Experiments

Condition	Series 1	Series 2	Series 3
1. Peak Linear Power, kW/ft	~ 30	45-50	~ 30
2. Fuel Composition	$(U_{0.8}Pu_{0.2})$ C, Solid-Solution, Sintered		
3. Fuel Uranium	^{235}U	^{235}U	^{235}U
4. Uranium Enrichment, %	93	97	93
5. Fuel Density, % theoretical	90	95	95
6. Pellet Diameter, in.	0.265 ± 0.002	——0.260 ± 0.002 ——	
7. Linear Density, %	81	82	82
8. Cladding[a]	——0.300 in. O.D. x 0.010 in. wall——		
9. Max. Cladding Temp., °F(°C)	1250(677)	1275(690)	1250(677)
10. Max. Fuel Centerline Temp. °F(°C)[b]	2130(1165)	2550(1400)	2100(1150)
11. Burnup	——————3 at% to 10 at% ——————		
12. Number of capsules	7	8	6

a The cladding is solution annealed Type 316 stainless steel.

b Centerline temperatures were calculated for a solid pellet.

TABLE 463-IV

STATUS OF SERIES -1, -2, AND -3 EXPERIMENTS

Capsule	Series	Subassembly	Current Burnup, at %	Status
K-36B	1	X142(X039)	3.7	awaiting insertion
K-37B	1	X086	3.2	interim exam
K-38B	1	X086	3.2	interim exam
K-39B	1	X086	3.2	interim exam
K-40B[a]	1	——	——	——
K-41B[a]	1	——	——	——
K-42B	1	X039	5.0	complete
K-43	3	X086	3.1	interim exam
K-44	3	X086	3.1	interim exam
K-45	3	X119	0.3	out[b]
K-46	3	X119	0.3	out[b]
K-47[a]	3	——	——	——
K-48[a]	3	——	——	——
K-49	2	X119	0.4	out[b]
K-50	2	X119	0.4	out[b]
K-51	2	X119	0.4	out[b]

a Capsules K-40B, -41B, -47, and -48 will be used as replacement capsules as needed.

b The X119 subassembly has been taken out of EBR-II due to the need for reactivity for higher priority experiments.

have been ordered from WADCO and will comply, as nearly as is current available, to the RDT-E-13-8T fuel element cladding specification.

To avoid the possibility of emphasizing atypically high cladding temperatures, in all cases where the peak cladding temperature is listed in Table 463-V as being near 625°C, duplicate tests will be run in which the peak cladding temperature is to the order of 575°C. This relatively large difference in cladding operating temperature stems from the variable coolant flow within the EBR-II subassembly. The twelve peripheral positions have a higher sodium coolant flow than the seven interior positions.

A 4N1 EBR-II reactor position has been selected for the experimental subassembly. It is planned that the experiments will start irradiation in an EBR-II N-19 type subassembly. After irradiation to a burnup of approximately 7 at%, five elements would be removed for destructive examination. The remaining elements plus five replacements would be reconstituted in an EBR-II E-19B type subassembly for continuation of irradiation to the goal burnup. It is estimated that the time to achieve the goal burnup, assuming a 50% duty factor for EBR-II and 3 months for the interim examination, will be 2.25 years after starting the irradiation. The scheduled starting time for the irradiation is June 1972. The serious priority difficulties associated with the EBR-II reactivity are not expected to affect these experiments as severely as the earlier series of experiments because, assuming a reactivity worth conversion for ^{239}Pu of 1.71 to equivalent grams of ^{235}U and considering only the total grams ^{235}U and ^{239}Pu, this experimental subassembly contains 3081 equivalent grams of ^{235}U. Therefore, the subassembly reactivity worth is 1.10 times the worth of an EBR-II driver fuel assembly.

The design of the apparatus for xenon tagging the element plenum gas for the nineteen element subassembly has been completed and fabrication started.

The fuel loading facility was utilized to load six standardization capsules with FFTF prototype fuel for the Safeguards Group.

TABLE 463-V

Description of Series 4 Experiments

Element Type	No. of Tests	Peak Heat Rate kW/ft	Peak Burnup at% (MWD/MTM)	Peak Cladding[b] Temperature °F (°C)	Peak Centerline[c] Temperature °F (°C)
1A	6	38.3	12.0 (108,000)	1167 (631)	1994 (1090)
1B	3	38.3	12.3 (107,400)	1167 (628)	1975 (1079)
3A	2	38.9	11.7 (102,600)	1060 (571)	1977 (1081)
3A	2	38.6	11.7 (102,600)	1197 (653)	2448 (1343)
3B	3	39.44	11.7 (107,600)	1181 (638)	2496 (1369)
4A	2	38.9	11.4 (100,000)	1078 (581)	2493 (1367)
4B	2	38.6	11.1 (97,200)	1068 (576)	2443 (1339)

a Type 1 is 95% dense $(U_{0.8}Pu_{0.2})C$, 80% smear density.
Type 2 is 95% dense $(U_{0.8}Pu_{0.2})C$, 85% smear density.
Type 3 is 95% dense $(U_{0.8}Pu_{0.2})N$, 80% smear density.
Type 4 is 95% dense $(U_{0.8}Pu_{0.2})N$, 85% smear density.
A refers to solution-Annealed Type 316 stainless steel.
B refers to 20% cold-worked Type 316 stainless steel.

b The nominal inside diameter cladding temperatures for the highest temperature element.

c The nominal centerline fuel temperature for the highest temperature element.

A tentative procedure for the handling of failed fuel elements at EBR-II was sent to ANL for comment.

Capsule K-36B was returned to EBR-II for reinsertion in subassembly X142.

C. TREAT Irradiation Testing

(J. F. Kerris, R. E. Alcouffe, D. G. Clifton, K. L. Walters, J. O. Barner)

In order to assess the behavior of (U, Pu) C and (U, Pu) N fueled elements under fast reactor accident conditions, transient irradiations will be conducted in the TREAT facility. Investigations will be conducted on both irradiated and unirradiated fuel pins to determine (1) the threshold power levels at which damage or failure occurs, (2) the effect of bond and cladding defects, and (3) the failure propagation mechanism in multipin assemblies.

A cooperative effort has been initiated with the United Nuclear Corporation in the area of TREAT testing. Four unfiltered experiments are planned. Two sodium bonded pins prepared by UNC will be tested: one irradiated and one unirradiated. Also, two UNC helium bonded pins will be examined; again, one irradiated and one unirradiated. Neutronic and heat transfer analysis of these experiments is being carried out.

The first experiments utilizing LASL fabricated fuel pins will be directed toward defining the threshold conditions at which boiling occurs in the sodium bond, and also determining the behavior of the thermal bond after the onset of boiling. These tests will be run in a

pressure vessel assembly incorporating a thermal neutron shield to provide for power generation and temperature distributions in the fuel that are more typical of fast reactor systems.

1. Neutronic Analysis

A series of two-dimensional calculations has been performed in order to determine the figure of merit (ratio of power density in the experimental fuel pin to power produced in the reactor) for various experiments. The results of the computations to date are shown in Table 463-VI for three experiments. Experiment UNC138A is a United Nuclear Corp. helium bonded, (U, Pu) C fuel pin, while UNC146A is a similar fuel pin except sodium bonded. The LASL experiment consists of a sodium-bonded mixed-carbide pin with some of the reactor thermal neutron flux screened out by a 0.010 in. natural gadolinum filter. The quantities presented in Table 463-VI are (1) the one-dimensional estimates, (2) the conventional two-dimensional diffusion theory estimates, and (3) the generalized two-dimensional diffusion estimate which uses as a trial solution the one-dimensional S_n computation. Note that, in the UNC138A case which has all three computations completed, the figure of merit difference between the two-dimensional results is -16% where the last number is taken as the final result. The anomalous result for the two-dimensional diffusion result for the LASL experiment is thought to be due to the inaccuracy in the diffusion flux through the gadolinum filter. This will be checked out with subsequent calculations.

2. Heat Transfer Analysis

Heat transfer calculations are being performed to predict the behavior of fuel pins during transient tests in the TREAT reactor with the CINDA-3G heat transfer code. Calculations are in progress using the space energy distribution functions obtained from neutronic analysis for various thermal neutron filters to assess the effect of the filter on the thermal behavior of the fuel pin. The results will be compared to the limiting cases of a uniform energy generation and an unfiltered test for which the fuel pin edge to center power ratio is 7.

Minor modifications of the one-dimensional heat transfer code were made to allow for gamma heating in the heat sink and steel of the capsule and to plot temperatures as an output option.

3. Stress Analysis

A subroutine for calculating stresses in the clad including plastic or viscoelastic behavior and accounting for internal pressure and axial loads has been added to the heat transfer code.

4. TREAT Capsule Design

Design work is in progress on the TREAT capsule for LASL tests. The TREAT capsule contains heaters for setting the fuel pin temperature prior to the test, thermocouples, thermal insulation, and the thermal neutron filter, all contained in a pressure vessel which replaces a fuel element in the TREAT reactor. An inner capsule containing the fuel pin to be tested is inserted into the TREAT capsule for the test.

A scale layout of a TREAT capsule for LASL tests has been prepared using capsule designs of other TREAT experimenters as a guide. The use of a thermal neutron filter and a pressure transducer to measure fuel pin pressures are innovations which require modifications in previous designs. The proposed LASL TREAT capsule design was discussed with the TREAT Project Manager during a recent visit to the TREAT reactor. No serious problems were found.

5. Test Instrumentation

Manufacturers have been contacted concerning thermocouples and heaters for the TREAT capsule. The items necessary are standard with a number of manufacturers so that no procurement problems are foreseen.

Representatives of Kamen Science Corporation were consulted about the use of their variable impedence pressure transducer to measure pressures in the fuel pin.

TABLE 463-VI

FIGURES OF MERIT FOR VARIOUS TREAT EXPERIMENTS

Experiment	Figures of Merit (10^4 W/cm^3/reactor W)		
	One-Dimensional	Two-Dimensional Diffusion	Two-Dimensional Transport
UNC138A	1.054	1.354	1.170
UNC146A	1.063	1.414	—
LASL	0.427	0.226	—

They can provide a transducer of approximately 1/2 in. O.D. with the appropriate mounting flanges to allow the transducer to be welded to the top of the fuel pin. The transducer has two coaxial leads (copper central conductor, MgO insulated, stainless steel sheathed) which can be terminated with a ceramic-to-metal seal terminal that allows a connection to flexible coaxial cable. Coaxial type leads must be maintained over the whole length of the pressure transducer leads. The purchase of electrical connectors with coaxial and conventional single pins is being investigated.

III. FUEL PROPERTY MEASUREMENTS

A. Differential Thermal Analysis of Irradiated Oxides

(J.G. Reavis, R. Brewer)

A cooperative program for which GE-Sunnyvale has furnished specimens of irradiated UO_2-PuO_2 to LASL for differential thermal analysis is proceeding. Five sealed tungsten capsules containing reference standards or fuel materials have been examined using the DTA apparatus in the hot cell. The results obtained for these samples are compared in Table 463-VII with results for two samples of NUMEC-B series fuel materials previously observed in the same apparatus. The temperatures listed in Table 463-VII were obtained by determining apparent arrest temperatures and adding window absorption corrections from a correction curve which has been in use for several months. The validity of these correction data is indicated by the agreement between the observed melting points of reference samples R-1 and R-2 and their respective literature values. Best literature values for melting points of Al_2O_3 and ZrO_2 are 2051°C and 2685°C, respectively.

TABLE 463-VII

DTA Observations in the Hot Cell Apparatus

Sample No.	Composition	O/M Ratio	Burnup, a/o	Arrest Temp., °C Solidus	Liquidus
R-1	Al_2O_3	----	----	2049	----
R-2	ZrO_2	----	----	2700	----
A-1	UO_2 - 25% PuO_2	1.96	0.0	2790	2840
FSB-7	UO_2 - 25% PuO_2	1.98	4.3	2755	2810
FOK-H	UO_2 - 20% PuO_2	2.00	5.4	> 2710[a]	----

a No solidus arrest was observed for sample FOK-H up to 2710°C, but the capsule leaked at a temperature somewhat greater than 2710°, resulting in termination of the experiment.

The solidus and liquidus temperatures of all UO_2-PuO_2 samples except FOK-H are based on multiple thermal cycles of one capsule of each batch of oxide. The "solidus" temperatures listed here may not be the temperatures of first liquid formation, since the irradiated samples may be expected to contain traces of fission product inclusions which may melt at lower temperatures. The reported solidus is the temperature of the first major thermal arrest. These arrests have the form typical of the melting of solid solutions. The liquidus temperatures were determined from arrests in cooling curves.

Only a minimum value can be given for the solidus temperature of FOK-H. When this sample was heated slightly higher than 2700°C, a pressure rise was noted in the system, and the induction-heated furnace arced. Later examination showed that a small amount of material had escaped from the capsule.

An error analysis program is being set up to allow mathematically precise statements to be made of uncertainties in observed temperatures. At this time, the chief value of this part of the program is to give guidance in selecting the optimum number of measurements to be made on reference materials as well as the irradiated samples. Exact uncertainties for the temperatures listed in Table 463-VII cannot be given until the statistical study is complete.

B. High Temperature Calorimetry of Irradiated Oxides

(David G. Clifton)

Enthalpy measurements are being made on Al_2O_3 in the hot cell, high temperature drop calorimeter. These will permit a correlation between the fairly well established enthalpy values for Al_2O_3 and the values reported recently for irradiated and unirradiated UO_2-20% PuO_2.

A sample of Standard Reference Material 720, synthetic sapphire (Al_2O_3), obtained from the National Bureau of Standards with an accompanying certificate giving its enthalpy for the temperature range from 273 to 2250°K, has been encapsulated in a standard tungsten capsule.

Table 463-VIII lists the enthalpy measurements that have been made to date at the respective temperatures given in column one. The third column gives interpolated NBS values for these same temperatures. The fourth column lists the percentage deviation of the observed values from the NBS values. It is evident that these observed values are lower than the NBS data by from 1 to 3%, this may indicate a systematic error in the measuring system.

TABLE 463-VIII

ENTHALPY OF Al_2O_3

T°C	$H_T-H_{25}°_C$, Cal/gm obs.	NBS	% Deviation
1305	349.9	358	-2.3
1407	381.3	389	-2.0
1494	410.7	417.5	-1.6
1595	444.2	448	-0.9
1687	465.2	478	-2.7
1799	499.2	514	-2.9
1889	534.1	543	-1.6

New electrical calibrations presently are being made to substantiate the energy equivalent of the calorimeter and a new series of observations for the window corrections for the pyrometer system are underway. A different pyrometer which has recently been calibrated at Sandia Laboratories is being used.

Discovery of this 1 to 3% deviation does not negate the previously reported enthalpy differences between the irradiated and unirradiated UO_2-20% PuO_2 NUMEC fuel; however, it does lend uncertainty to arguments based on the comparison of the hot cell data taken on the NUMEC samples with those reported by Ogard that were taken with a different calorimeter.

A series of experiments were attempted on another encapsulated sample of Al_2O_3. The material was cycled through the melting point of Al_2O_3, 2324°K, several times while pyrometer readings were taken as a function of time; the purpose being to try to observe thermal arrests due to melting and freezing and consequently obtaining a pyrometer correction factor check at a known high temperature point. The data acquired were marginal but indicated that the corrected reading may be as much as 25°C high. The difficulty was caused by deformation of the tungsten capsule because of its being overloaded. The density change of Al_2O_3 from room temperature through melting is so large (ρ 25°C = 4gm/cm³; ρ 2051°C = 2.5 gm/cm³) that severe internal pressures resulted, and then the deformed capsule became misaligned so that the black body hole could not be used.

Calculations based upon the smaller quantity of NBS standard Al_2O_3 sample show that it would now be possible to repeat the above experiment; however, as a precautionary measure, enthalpy valves for the Al_2O_3 shall first be acquired below the melting point.

IV. PUBLICATIONS

1. M. W. Shupe, J. G. Reavis, and J. L. Green, "The Synthesis, Fabrication and Characterization of Solid Solution, Uranium-Plutonium Carbide Fuels", presented at the 162nd National Meeting of the American Chemical Society, Washington, D.C., September 12-17, 1971.

2. J. O. Barner and J. C. Clifford, "The Chemical Effects of High Burnup in High Purity, Solid Solution, Uranium-Plutonium Carbide Fuel Elements", presented at the 162nd National Meeting of the American Chemical Society, Washington, D.C., September 12-17, 1971.

3. K. W. R. Johnson and J. F. Kerrisk "Thermal Diffusivity of Molybdenum and Tungsten Between 20°C and 2000°C", Thermal Conductivity-Proceedings of the Eleventh International Conference, (Ed. R. U. Acton, P. Wagner, and A. V. Houghton, III) pp. 3-4, 1971.

4. J. F. Kerrisk, "Steady-State Approximation in Thermal Diffusivity Measurements on Heterogeneous Materials", Thermal Conductivity-Proceedings of the Eleventh International Conference, (Ed. R. U. Acton, P. Wagner, and A. V. Houghton, III) pp. 143-144, 1971

PROJECT 472

ANALYTICAL STANDARDS FOR FAST BREEDER REACTOR OXIDE FUEL

Person in Charge: R. D. Baker
Principal Investigator: C. F. Metz

I. INTRODUCTION

Necessary to the development of the high quality fuels and control rods required by the LMFBR program are highly reliable analytical methods for the chemical characterization of the source materials and the pellet products and for the examination of irradiated specimens.

The immediate objectives of this project are (1) the evaluation of existing methods for the chemical characterization of boron carbide to be used as the absorber for FFTF control rods; (2) the development of improved methods, as required, for mixed oxide fuels, advanced fuels, and boron carbide; (3) the preparation of extremely well characterized calibration materials for the various chemical specification analyses performed at the fuel producers' and buyer's facilities for the above materials; (4) the preparation of continuously updated compilations of analytical methods for the above materials; (5) the development of quality assurance programs for chemical specification sampling and analysis of the above materials; (6) the preparation of quality control samples used for the continuous surveillance of analytical chemistry laboratory operations during periods of fuel pin and control rod production; (7) serve as a "neutral" referee laboratory, as may be required, to analyze samples in dispute between a producer and buyer; and (8) measure the tritium content of irradiated fuel pins processed at LASL (under the 07401 Program) to establish the degree of diffusion of this gas through the fuel cladding. These objectives will be extended, as required, to the LMFBR demonstration plants.

Other objectives, concerned with irradiated fuel examination, are (1) development of fuel burnup measurement methods based on conventional and spark source mass spectrometric determinations of actinide and fission product isotopes; (2) development of faster fuel burnup measurement methods based on chemical analysis techniques for use for larger routine sample loads; (3) correlation of nondestructive gamma ray scans of whole fuel pins with destructive burnup measurements to assess the reliability of gamma scanning for measurement of burnup; (4) correlation of burnup measurements with other measurement techniques including electron microprobe and metallographic examinations to assess irradiation behavior of LMFBR fuels; (5) development of analytical methods for impurity and fission gases in pre- and postirradiated fuels to provide for studies of fuel gas retention properties and cladding stability; and (6) application of the ion microprobe analysis technique to study migration mechanisms in irradiated fuels.

II. ANALYTICAL CHEMISTRY PROGRAM FOR BORON CARBIDE

The proposed neutron absorber material for LMFBR/FFTF control rods is boron carbide pellets. A coordinated program with HEDL is underway to establish the status of analytical methods for the chemical characterization of boron carbide and to develop improved methods as necessary.

A. Status of Analytical Methods
(J. E. Rein, C. F. Metz)

A round robin analytical chemistry program was completed in which presently available analytical methods[1] for seven chemical specifications were evaluated. The major findings and status of the methods are summarized in Table 472-1. Certain methods will be modified on a high priority basis for intended use in a vendor qualification program administered by WADCO. These

Table 472 - 1 STATUS OF METHODS FOR CHEMICAL SPECIFICATION ANALYSES OF BORON CARBIDE BASED ON AN INITIAL ROUND ROBIN PROGRAM

Specification	Status	Future Effort
Total Boron	1. Present method satisfactory for vendor qualification. 2. High results can be caused by adverse effect of amphoteric metal impurities (such as aluminum).	1. Revise method to minimize effect of amphoteric metal impurities. 2. Develop (on long term basis) alternate method based on sealed tube dissolution of samples and separation of metal impurities prior to mannitol potentiometric titration.
Total Carbon	1. Present method satisfactory for vendor qualification. 2. Alternate faster method using commercial equipment also satisfactory.	Other laboratories evaluate alternate method.
Isotopic Boron	1. Present method satisfactory for vendor qualification. 2. Alternate faster method also satisfactory.	Other laboratories evaluate alternate method.
Soluble Boron	1. Improvement of present method desirable for vendor qualification. 2. Significant between-laboratory difference attributed to effect of amphoteric metal impurities. 3. Boron species determined by method are uncertain.	1. Revise method to minimize amphoteric metal effect. 2. Develop (on high priority basis) alternate methods for determination of the solubilized boron. 3. Investigate (on long term basis) the boron species determined by method.
Soluble Carbon	1. Apparent high results obtained by two of the three laboratories attributed to use of modified apparatus. 2. Carbon species determined by method are uncertain.	1. Investigate (on high priority basis) cause for high results. 2. Investigate (on long term basis) alternate methods and the carbon species behavior.
Chloride and Fluoride	1. Improvement of present method desirable for vendor qualification. 2. Alternate method appeared to give satisfactory results.	1. Other laboratories evaluate alternate method on high priority basis. 2. LASL investigate (on long term basis) techniques to improve reliability of method.
Metal Impurities	Improvement of present emission spectrographic method desirable for vendor qualification.	1. Complete development (on high priority basis) of modified method. 2. Investigate (on long term basis) an alternative method.

modified methods will be evaluated by a second round robin program planned for December, 1971 - January, 1972. The round robin program results also gave direction to a longer term study for the development of improved methods. Further information concerning these methods is given in later sections.

B. Studies and Improvements of Analytical Methods

1. Chloride and Fluoride

(T. K. Marshall, R. G. Bryan, G. R. Waterbury)

Proposed methods for the determination of chloride and fluoride use pyrohydrolysis to remove the halogens from the remainder of the sample as HCl and HF respectively which are then measured spectrophotometrically, titrimetrically, or by a specific ion electrode. As conditions for the pyrohydrolysis are not unquestionably established, two sets of conditions were tested.

Under the first set of conditions, 1 g of powdered B_4C, to which had been added known quantities of chloride and fluoride, was mixed with 4 g of U_3O_8 and pyrohydrolized 20 min at 850°C in a flow of air which had been moistened by bubbling through water at 50°C. Under the second set of conditions, a similarly prepared sample was pyrohydrolyzed at 1000°C in a flow of Ar moistened by bubbling through boiling water. The flow rate produced 8 ml of condensate in 15 min. All pyrohydrolyses were done in an all-Ni reaction tube using Ni boats. The fluoride was measured in a 1-ml aliquot of the condensate using a specific ion electrode. The chloride in the remainder of the condensate was reacted with $Hg(CNS)_2$ and Fe^{+3} to form $Fe(CNS)_3$ which was measured spectrometrically at a wavelength of 460 nm.

The first set of pyrohydrolysis conditions resulted in recoveries of less than 60% of the added quantities of the halogens, and subsequent blanks were high. The second set of conditions produced recoveries between 95 and 100% from either U_3O_8 of a mixture of 1 g of B_4C and 4 g of U_3O_8. Limited data indicated that the reproducibilities of the measurements of chloride and fluoride added to B_4C were not significantly different than obtained in analyzing oxide fuel samples. The second set of pyrohydrolysis conditions were used in subsequent analyses for halides in B_4C.

2. Spectrographic Methods
(O. R. Simi, R. T. Phelps)

An investigation of possible areas for improvement in tentative method No. 20.4 described in report HEDL TME-71-34 was started. It was observed that visual differences could be seen between the arcing behavior of samples and standards. This attributed to the fact the matrices were not the same. The addition of B_4C to the standards to make them more similar chemically to the sample lessened the degree of difference between the arcing behavior of standards and sample. Additional improvements will be sought if a supply of high-purity B_4C can be obtained. Consideration is being given also to chemically changing the form of the sample prior to arcing in order to make more similar the arcing behavior of standards and samples.

An improved list of analytical spectral lines was selected for use by each laboratory in future round robins and will be included as a part of the recommended method as finally written.

3. Determination of Soluble Boron
(R. D. Gardner, Al Zerwekh, A. L. Henicksman, W. H. Ashley)

Attempts to improve the precision by using atomic absorption were not successful because no sufficiently sensitive line could be found. Flame emission spectrometry proved to be about 100 times more sensitive for boron, but it was subject to interference effects from the impurity elements. The use of the leanest possible nitrous oxide-acetylene flame improved that situation, making small amounts of the impurities tolerable. Batchwise treatment of small aliquots of the boron extracts with Dowex 50 reduced the impurities sufficiently. Known solutions containing boron and all of the impurity elements reported in the round robin sample at 0.5% level were analyzed with an average recovery of 99.9% and a relative standard deviation of 2.7%. At the 0.2% level the recoveries averaged 103.5% with a relative standard deviation of 3.9%. In addition, a previously analyzed material of good purity (B_4C-33) was analyzed by the new procedure, with excellent agreement with the previous soluble boron values by titration. The reliability of the cation exchange treatment would be improved by column operation, and will be tried. If it is not satisfactory, a possible variation also exists in the extraction with methyl isobutyl ketone of a BF_4^- complex, described in the literature.

It was reported previously the CO_2 was detected in the off gas from the nitric acid extraction. There seemed to be no likely source for this CO_2 except the boron carbide of the sample. In the course of the work on B_4C-33 just described, some samples were digested overnight, a total of 16 instead of the usual 4 h. The hydrochloric acid extractions showed no change, containing 0.15% boron after both periods. However, the nitric acid extraction in 4 h contained 0.55% boron and after 16 h 1.28%. This raises considerable doubt as to the usefulness of the nitric acid method for determining free boron. This investigation will be continued.

III. ANALYTICAL CHEMISTRY PROGRAM FOR LMFBR/FFTF FUEL

A. Calibration Materials and Quality Control Samples
(J. E. Rein, R. K. Zeigler, R. T. Phelps, C. F. Metz)

As discussed in the previous progress report[2] powder blends of metal and nonmetal impurities in matrices of uranium-plutonium mixed oxide, uranium oxide, and plutonium oxide have been prepared for use as calibration blends and quality control samples during periods of LMFBR/FFTF fuel productions. Extensive sampling and analysis has verified the accuracy and homogeneity of the blends. Mixed oxide pellets also will be used as quality control samples and a batch has been characterized for this use based on careful analyses.

In cooperation with WADCO, a final plan has been developed for the use of these materials in the fuel pin vendor qualification program scheduled to start next quarter. In accordance with this plan, the materials are being placed in labeled ampules in a manner such that WADCO can distribute them to the vendors and its own laboratory with no further packaging necessary. Recommended limits for the quality control samples have been calculated and will be supplied to the Quality Assurance Section at WADCO on a "company confidential" basis.

B. Development of Analytical Methods

1. Fuel Burnup Measurement
(R. M. Abernathey, J. E. Rein)

At the request of DRDT, a document is being prepared which reviews the status of chemical methods for fuel burnup determination applied to the FBR program. This document, being prepared in cooperation with the Allied Chemical Corporation (Idaho Falls, Idaho) and the Argonne National Laboratory, discusses techniques of burnup analysis, criteria for selection of burnup monitors, present limitations of the nuclear data applied to burnup analysis, and the experimental programs in progress and planned by ACC, ANL, and LASL to develop more reliable nuclear data and chemical methods for the accurate determination of burnup in all types of FBR fuels.

The first draft of this document, planned for world distribution, has been completed and final revision has been started. Completion is estimated by January, 1972.

2. Tritium Measurement in Irradiated Fuel
(R. M. Abernathey, G. M. Matlack, J. E. Rein)

Environmental considerations require a knowledge of the distribution of the tritium produced in reactor fuel by ternary fission. The experimental LMFBR fuel capsules undergoing postirradiation examination at LASL under the 401 program provide a potential source of unique information concerning the distribution of tritium. Tritium has been indicated to diffuse through stainless steel cladding at high operating temperatures and/or high linear heat rating[3]. These capsules, being double-contained, offer the possibility of measuring the tritium that has penetrated the inner cladding, as well as that retained in the fuel and embedded in the cladding.

The measurement techniques chosen are essentially those used at Vallecitos Nuclear Center[4] for the examination of Zircaloy-clad fuel. Liquid scintillation counting is planned for all determinations. Tritium retained in the fuel will be measured in a distilled aliquot of the dissolved fuel solution. Tritium in the cladding will be determined by vacuum outgassing and conversion to water or by combustion in oxygen. Gaseous tritium will be determined by oxidation, (by CuO at 700°C or by O_2-hot filament).

3. O/M Atom Ratios
(J. W. Dahlby, G. R. Waterbury)

Investigation of analysis conditions in the thermogravimetric measurement of O/M atom ratios is being continued to provide a better understanding of the factors influencing the results. In the recommended method, the dried sample is oxidized at 1000°C in air and then quantitatively reduced to the stoichiometric dioxide in a dried 94% He-6% H_2 gas mixture at 1000°C for 6 h. The reducing gas is dried in a 6 in. tower of $Mg(ClO_4)_2$ before coming in contact with the sample. Analysis with a sensitive moisture analyzer showed that the dried gas contained < 1 ppm of water. When the reaction furnace was heated to 1000°C with no (U, Pu)O_2 sample present, the water content of the effluent gas slowly increased to 2-3 ppm over a 6 h period. This slow increase in indicated water content could result from either a small quantity of O_2 in the gas or the apparatus that reacts with the H_2 at elevated temperatures, or from the moisture analyzer being slightly sensitive to H_2. The 2-3 ppm H_2O in the effluent gas was taken as a blank or baseline level.

The effluent gas was then monitored during the reduction of a 5-g sample of (U,Pu) oxide to the stoichiometric dioxide. Less than 1 min after the H_2 flow started, the water content increased very rapidly off scale (> 1000 ppm), remained there for about 11 min, and then decreased swiftly at about 14 min to 180 ppm. The water content of the gas then decreased at a slower rate to 46 ppm in 1 h, 13 ppm in 3 h, and 2 ppm in 7 h. These data show that most of the reaction takes place during the first 15 min. The small indicated water content in the effluent gas after this time may be due to small amounts of unreacted sample reacting slowly or to a slow "recovery" rate of the moisture analyzer after being exposed to large amounts of water. Moisture in the reducing gas does not seem to be a problem in this method.

IV. REFERENCES

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4. L. N. Grossman and J. O. Hegland, Report GEAP-12205, June 1971.

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