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A PROGRESS REPORT

Quarterly Report on the

Advanced Plutonium Fuels Program

January 1 to March 31, 1972

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

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A Progress Report
UC-80 AND FAST REACTOR REPORT
SPECIAL DISTRIBUTION
ISSUED: June 1972

Quarterly Report on the

Advanced Plutonium Fuels Program

January 1 to March 31, 1972*

Compiled by

R. D. Baker

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*This work supported by the Division of Reactor Development and Technology, U. S. Atomic Energy Commission.

FOREWORD

This is the 23rd 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.

TABLE OF CONTENTS

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 of this cell has continued to be maintained by the recirculating purifier system at typical concentrations of 2.5 to 3.5 ppm O_2. The concentration of H_2O has risen slowly during the report period and ranged from 1.5 to 7.5 ppm. A reduction in the ultimate vacuum capability of the regeneration system vacuum pump has been determined as the cause of the increased H_2O levels. The vacuum pump will be overhauled in the near future to correct this problem.

2. Metallography Cells. The atmosphere of the two metallography cells was maintained by a combination Ar once-through purge for control of the O_2 concentrations and operation of the RSD* portion of the recirculating purifier for control of the H_2O concentrations. (Maintenance of the O_2 levels by the KBM* portion of the recirculating purifier has been suspended pending installation of a cold trap system to remove solvents from the atmosphere.) Concentrations ranged from 50 to 2000 ppm O_2 and from 3 to 15 ppm H_2O during the report period.

Two experimental PVC-fabricated master-slave manipulator boots were installed on December 1, 1971 in one of the cells. One of the boots is still in service and

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*Designations of proprietary chemicals

has shown no significant deterioration. The other boot suffered a tear in February, not attributable to solvent exposure damage, and required replacement. As a result of the observations of several new techniques in the fabrication of polyurethane components for manipulator boots during a visit at the Central Research Laboratory in March, a Plastics Group at LASL will again attempt to fabricate an experimental polyurethane boot for the master-slave manipulators in use at the Wing 9 Facility.

3. Metallograph Blister Assembly. A shroud enclosing the Bausch and Lomb metallograph in the new blister assembly has been designed and a local work order issued for fabrication from plastic.

During disassembly of the transfer tunnel connecting the metallography cell to the blister, several parts were discovered that permitted considerable air leakage into the inert atmosphere system. The parts were redesigned to eliminate the possibility of leakage in future operations.

The system for providing inert atmosphere in the new blister has been installed. Provisions were made for a once-through Ar purge or recirculation with the purifier which supplies the argon to the two metallography cells.

B. Master-Slave Manipulator Decontamination and Repair

(P. A. Mason, J. M. Ledbetter, O. Serna, G. R. Brewer, R. F. Velkinburg)

The program for disassembly and complete overhaul of the master-slave manipulators was started. Approximately one-third of the manipulators requiring service have now been completed.

During this period it has been possible to provide all personnel with experience in decontamination, disassembly, and maintenance procedures. Approximately 40 to 60 man-hours were required for the complete overhaul of a manipulator.

Tentative selections of personnel have been made to provide a routine maintenance and inspection program which is planned to begin July 1.

C. Shipping Casks

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

The small cask (DOT-SP 6421), designed to ship short sections of fuel pins off-site, was received in February and is now ready for use. A third "Rover" cask was received, and modifications were accomplished in the lid and lid fasteners (special nuts) to insure an adequate seal for shipping. These modifications were made locally at the LASL and checked out for seal integrity.

A LASL Engineering group has been assigned the responsibility of implementing gasket and closure modifications to all ten "Rover" casks to comply with the requirements of the recently modified DOT permit.

D. New Metallograph Blister

(D. D. Jeffries, K. A. Johnson, C. D. Montgomery, J. M. Ledbetter, G. R. Brewer, T. Romanik, R. F. Velkinburg, J. B. Weber)

Removal of the old metallograph blister installation and the final "in place" assembly of the new blister was started March 20 and is expected to be completed in about six weeks. A special removable hatch, sealed by means of a gasket, has been provided in the top for possible changes of the ion etcher equipment which has not yet been completely defined. Special plumbing and electrical provisions have been made underneath the box to fulfill the general requirements of the ion etcher.

The drive mechanism and the transfer tunnel connecting the metallography cell to the blister have been installed, sealed, and leak-checked. The newly designed and fabricated sealed door installation, which replaces the former large gate valve, has been checked out and proved superior to the previous installation.

The new telescoping mechanism for the side bag-out port is complete except for the bellows seal which is expected by April 6.

The shielding modules, including the Bausch and Lomb metallograph unit, are being installed. The Bausch and Lomb module will then be removed for optical alignment and the installation of a new stage by a Service Engineer.

Installation of the new Leitz metallograph will be started the first week of April. The Factory Engineer will arrive about mid-April for final check-out.

E. New Mechanical Profilometer

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

Work continues on the design of a new mechanical profilometer to be used as a backup instrument for the Electro-Optical unit.

The present design will be changed to eliminate the use of a 4-jaw scroll chuck which has not been found commercially and which is too expensive to fabricate.

F. Butyl Acetate Removal System

(G. S. Dow, M. E. Lazarus)

Design of a chill trap for butyl acetate removal is now 90% complete. The heat exchanger, which is 100% copper and commercially available, is on hand. The compressor unit will be ordered in the near future.

G. Bausch and Lomb Optical Gage

(M. E. Lazarus, T. Romanik, J. R. Trujillo)

Fabrication is nearly complete on the modification of a Bausch and Lomb Optical gage, and the equipment should be ready for check-out and use next month.

H. Radiography Cask

(C. D. Montgomery, R. F. D. Griffiths, J. R. Trujillo)

Design has been completed and fabrication started on a new cask for use in Betatron radiography of 61-inch-long pins.

The design was made in accordance with the Department of Transportation requirements. Approval of a Special Permit has been requested.

A horizontal pallet with trunnions is being provided in the event the cask is used for off-site shipments. It is anticipated that the cask would be completed and available for use by July 1972.

Modifications to the room at the Betatron site to accommodate the increased height of the cask are proceeding concurrently with the cask fabrication.

I. Pin Handling Mechanism for Betatron Radiography

(C. D. Montgomery, T. Romanik, J. R. Trujillo)

A vertical transport device for removal of the pin from the radiography cask (Item H above) is in design. This improved mechanism will allow the incremental raising of the pin in a precise manner. This mechanism is mounted on three wheels and can be rolled up and attached to the cask to provide the stability required.

J. Revised Alpha Box Design

(P. A. Mason, C. D. Montgomery)

Conceptual design work on a revised alpha box has been completed. Revisions include relocation of the 7-inch can transfer system, relocation of the glove port stations with enlarged viewing windows, incorporation of a remotely replaceable periscope viewing window, and wider latitude in adjusting the location of the mercury vapor light well assemblies. Preliminary design work was completed on a pressurized, double-seal system for providing an ultra-high purity inert atmosphere in an alpha box to see what modifications would have to be made on the basic alpha box design. Preliminary design work was also completed on a chilled water cooler for controlling the temperature of the inert atmosphere in an alpha box.

K. Scanning Electron Microscopy

(K. A. Johnson, J. L. Lehmann)

The EDX accessory has been returned to the manufacturer for upgrading to include higher counting rates and better resolution.

L. Microstructural Analysis Equipment and Developments

(J. H. Bender, K. A. Johnson, J. L. Lehmann, K. L. Walters, L. W. Reese)

1. A larger ion gun has been fabricated to provide higher beam currents needed to shorten etching times. This larger gun has stability problems which are being worked out.

2. The high pressure specimen mounting system is operational for unirradiated materials and is giving excellent results when used with porous ceramic materials such as mixed oxide pellets.

3. The updated computer code IMAGE VIII has been applied to the HEDL round-robin mixed oxide specimens and works well.

4. The installation engineering drawings for the print processor darkroom have been completed.

III. HOT CELL FACILITY AT DP WEST

A. Structure and Equipment

(F. J. Fitzgibbon, M. E. Lazarus, J. M. Ledbetter, C. D. Montgomery, J. R. Phillips, J. R. Trujillo, R. F. Velkinburg)

Most of the major items for building modifications have now been finsihed. The air conditioning, power, and light services were completed in the balcony where it is proposed to handle the data processing equipment. A trailer is also being investigated concurrently in the event additional space and facilities are required.

B. Hot Cell Equipment

1. Gamma Scanning Equipment. All of the lead-tungsten collimators have been radiographed and accepted. Installation of the mechanical and electrical equipment in the cells is now about 80% complete.

2. Electro-Optical Profilometer. The periscope shielding has been installed and the equipment is now ready for measurements on irradiated fuel elements at a slow speed of 12 inches per minute. Data acquisition problems have not been solved at high speed (60 inches per minute), and a considerable amount of work may be necessary to obtain operation at this speed.

Safety switches have been installed to prevent damage to the mechanical stage in case of most operator errors.

A computer program is now being compiled to translate the data on magnetic tape to a plot on 35 mm film. When completed, the program should be able to plot and analyze the data.

It is planned to use this new profilometer in obtaining continuous diameter measurements on 19 unirradiated pins from Gulf United during the second week in April.

3. Macro-Camera System. Modifications to the camera stand have been completed and the system is now ready for operation.

4. Pulsed Eddy Current Scanner. The mechanical stage for the scanner is now in fabrication. The four-channel recorder, which was ordered from excess equipment, has been received and checked out. Three of the four channels work properly, the fourth channel will need repair and will probably require replacement of some electron tubes (in the amplifier) which are not LASL stock items.

IV. METHODS OF ANALYSIS

A. Gamma Scanning System for DP West

(J. R. Phillips, G. H. Mottaz, J. N. Quintana)

The new precision scanning mechanism was installed in the gamma scanning hot cell. The stepping motors and shaft encoder were phased and the preliminary testing of the mechanism was begun. The anticoincidence shield was installed following two modifications that were necessary to permit the proper alignment of the collimators and the detector system.

The preliminary design has been completed for an adapter on the scanning mechanism for centering the fuel pins. The fuel pin must be centered with respect to the collimating slit because the source response varies as a function of position. The adapter should significantly increase the precision of the gamma scan results and permit the comparison of results obtained for different fuel pins.

Incorporation of a secondary cobalt-60 standard in the sample holder is being considered to provide a width and length standard, an energy standard, and a secondary source standard that would be easily accessible for routine calibration.

B. Determination of U and Pu in Irradiated Fuels

(J. W. Dahlby)

Controlled potential coulometry has been shown to be satisfactory for determining U and Pu in irradiated fuels having undergone up to 6 at.% burnup. The U is measured by integrating the current while reducing U(VI) to U(IV), and subtracting a blank. The Pu is determined by electrically oxidizing the Pu(III) to Pu(IV), and then reducing the Pu(IV) to Pu(III). This oxidation-reduction cycle is repeated until successive integrated currents agree within 2 Mv or 2 μg of Pu. Separation of the U and Pu from each other or from the fission products is not required for samples having less than 6% burnup. At higher burnups, the increased radioactivity and fission products adversely affect the analysis, and a separation of the U and Pu from the highly radioactive fission products is necessary.

Precipitation separations are being investigated first because they are simple, quick, and require a minimum amount of equipment. Separation of U and Pu from fission products using a fluoride precipitation was unsuccessful because approximately 1% of the U was lost. Studies were then made of the separation of U individually from Pu and fission products. Precipitation of U as the hydroxide and then redissolving the U in basic $(NH_4)_2CO_3$ was nearly quantitative. The average recovery for U from a mixture of unirradiated 75% U-25% Pu was 99.77 ± 0.06% for seven determinations. Although this recovery was satisfactory, only about 67% of the β-γ emitting fission isotopes were removed. Better decontamination factors were achieved by precipitating U with NH_4OH, and then selectively dissolving the U in basic NH_2OH. Approximately 75% of the β-γ active fission products were removed using NH_4F-HF as the U solvent and > 95% were removed when the precipitate was dissolved in basic NH_2OH. The recoveries of U following these separations are being measured.

In addition, a technique was tried which reportedly separates U from many other elements by extracting the U into N-butylaniline and then back extracting it into water.[1] In applying this separation to one irradiated sample, > 95% of the β-γ active material was separated from the U fraction. The recovery of the U is now being measured.

C. The Determination of Free C, Total C, and H_2 in (UPu)C and (U, Pu)O_2

(T. K. Marshall)

The measurement of C and H on highly irradiated reactor materials was tested by repeatedly analyzing stainless steel cladding from a fuel pin having about 10% burn-up. The C and H were measured as CO_2 and H_2O, respectively, after burning the samples at 1000°C in pure O_2. The cladding was found to contain 55 ± 30 ppm of hydrogen and 725 ± 70 ppm of carbon. Difficulties were not experienced because of the high burn-up, but the small amounts of sample available adversely affected the precision. Additional test analyses are planned.

Modification of a LECO Low Carbon Analyzer for installation in the hot cell is in progress. At the present time a switch is being prepared to enable use of an existing RF generator in the cell for heating samples.

D. Analytical Chemistry Quality Assurance Program

(J. W. Dahlby, G. R. Waterbury, O. R. Simi,
C. S. MacDougall, J. Bubernak, W. Zelezny,
J. R. Phillips)

To ensure that approved standard operating procedures are followed in all analyses and tests performed on irradiated materials, documents are being written describing the scope and critical steps of each operation. These documents stress the calibration procedures, the standards used for each measurement, and the sensitive conditions for each analysis or test. Approximately twenty tentative procedures and a quality assurance plan for analytical chemistry have been written. These documents are being reviewed, edited, approved by the Quality Assurance representative, and typed. They will be available for distribution to experimenters requesting diagnostic examinations of irradiated capsules and fuel pins.

V. REQUESTS FROM DRDT

A. Examination of Unirradiated Fuels

(J. H. Bender, D. D. Jeffries, K. A. Johnson,
J. L. Lehmann, L. W. Reese)

Mixed Oxide Round Robin. In cooperation with HEDL, LASL is participating in an optical microscopy round robin, and the laboratory work is completed. The darkroom work and data reduction are almost complete. One set of round-robin samples was also processed in the hot cells to have a comparison with a set of specimens polished in the glovebox system.

B. Examination of Irradiated Materials

R. M. Abernathey, K. A. Johnson, E. D. Loughran,
R. A. Morris, J. R. Phillips, J. W. Schulte,
G. R. Waterbury, W. F. Zelezny)

General Electric Company. On February 14, 1972, four irradiated fuel assemblies were received from GE-Vallecitos. Examinations performed on these assemblies are described in Table 401-I and Table 401-II.

TABLE 401-I

POST IRRADIATION EXAMINATION OF CAPSULES FROM GENERAL ELECTRIC

Examination	Capsule Identity
1. Visual Inspection	F4E, F4A
2. Preliminary Measurement	F4E, F4A
3. Photography (Full Length)	F4E, F4A
4. Radiography	F4E, F4A

TABLE 401-II

POSTIRRADIATION EXAMINATION OF PINS FROM GENERAL ELECTRIC

Examination	Pin Identity
1. Visual Inspection	F9C-13, F12P, F12Q
2. Photography (Full Length)	F9C-13, F12P, F12Q
3. Photography (Incremental)	F9C-13, F12P, F12Q
4. Radiography	F9C-13, F12P, F12Q

Four gross gamma scans and one complete spectral scan were made on GE-F4-E.

A meeting was held with GE personnel on March 15 to firm up the requirements of the examinations remaining to be completed on the five pins which were received in February.

Gulf United Nuclear Fuels Corporation. Examinations and operations performed on Gulf United materials are described in Table 401-III.

The cladding was removed from pins UNC-194 and -200 using established procedures. These pins were known to be breached when fission gas was found in the capsule; the two pins were therefore opened in the alpha box.

TABLE 401-III

POSTIRRADIATION EXAMINATION OF PINS FROM GULF UNITED

Examination	UNC Pin Identity
1. Gamma Scanning	
2. Fission Gas Sampling and Analysis	187, 189, 191, 192, 194, 195, 197, 198, 200, 206, 208
3. Profilometry	187, 189, 191, 192, 194, 195, 197, 198, 200, 206, 208
4. Photography (Incremental)	194, 200

Fuel-clad specimens from UNC-92, -96, -99, -104, -107, -108, -109, -111, -112, were dissolved, and burnup measurements were made.

Disintegration rates for ^{54}Mn were determined on iron flux wires from the following five fuel pins: UNC-107, -108, -109, -111, and -112.

Microstructural examinations have been completed on specimens from the pins tabulated in Table 401-IV.

TABLE 401-IV

MICROSTRUCTURAL EXAMINATION OF PINS FROM GULF UNITED

Pin No.	Clad	Fuel-Clad
UNC- 99	1	4
UNC-104	1	4
UNC-107	1	3
UNC-108	1	1
UNC-109	1	3
UNC-111	1	2
UNC-112	1	1

These examinations in an argon atmosphere included macrophotography, alpha and beta-gamma autoradiography, and optical microscopy (including mosaics).

Four specimens were prepared for examination with the shielded electron microprobe including pre- and post-EMX photomicroscopy.

A ruptured region of a mixed carbide fuel sample, UNC-107 H, which had been helium bonded to stainless steel cladding, was examined using the shielded microprobe. Two other samples, UNC-97 H and UNC-96 H, were also examined using the shielded microprobe.

Hanford Engineering Development Laboratory. Eleven pins from the PNL-17 series were received on February 22, 1972. The examinations made on these and other HEDL pins are described in Table 401-V.

Gamma scanning was applied to the nondestructive examination of the ten fuel pins tabulated in Table 401-V.

TABLE 401-V

GAMMA SCANNING OF HEDL PINS

Fuel Pin Number	Number Gamma Scans	
	Gross	Complete Spectral
HEDL-P-17A-5	4	-
HEDL-P-17A-16	4	-
HEDL-P-17A-33	4	1
HEDL-P-17A-17	4	-
HEDL-P-17A-18	4	-
HEDL-P-17A-19	5	1
HEDL-P-17A-20	4	-
HEDL-P-17A-26	4	-
HEDL-P-17A-29	7	1
HEDL-P-17A-30	4	-

Additional postirradiation examinations conducted are shown in Table 401-VI.

Density measurements were made on four cladding specimens from each of PNL-17-7 and PNL-17-33.

The silicon carbide temperature monitors from PNL-17-7 and PNL-17-33 were shipped to the sponsor.

The pin gas samples from PNL-17-7 and PNL-17-33 were analyzed mass spectrometrically, and the burnup of the fuel in each of these two pins was also determined.

TABLE 401-VI

POSTIRRADIATION EXAMINATION OF PINS FROM HEDL

	Examination	PNL Pin Identity
1.	Visual Inspection and Preliminary Measurements	P-17A-5, -16, -17, -18, -19, -20, -26, -27, -29, -31, -33
2.	Photography (Full Length)	P-17A-5, -16, -17, -18, -19, -20, -26, -27, -29, -31, -33
3.	Radiography	P-17A-5, -16, -17, -18, -19, -20, -26, -29, -31, -33
4.	Photography (Incremental w/wire wrap and w/o wire wrap)	P-17A-5, -16, -17, -18, -19, -20, -26, -27, -29, -31, -33
5.	Removal of Wire Wrap	P-17A-5, -16, -17, -18, -19, -20, -26, -27, -29, -31, -33
6.	Diameter Measurements (by micrometer on bent pin)	P-17A-27
7.	Fission Gas Sampling	P-17A-5, -16, -17, -18, PNL-17-7, PNL-17-33
8.	Profilometry	PNL-17-7, -33
9.	Sectioning	PNL-17-7, -33

Microstructural examinations were completed on the specimens tabulated below in Table 401-VII.

TABLE 401-VII

MICROSTRUCTURAL EXAMINATION
OF HEDL SPECIMENS

	No. of Specimens			
Pin No.	Clad	Welds	Brazes	Fuel-Clad
PNL-17-7	1	2	1	2
PNL-17-33	1	2	1	2

These examinations in argon atmosphere included macrophotography, alpha and beta-gamma autoradiography, and optical microscopy (including mosaics).

Pin P-17A-27 was damaged in handling during the initial examination period. The damage consisted of a 45° bend in the plenum area 6-1/2 inches below the top of the pin and a 3-inch bow from that point to the bottom of the pin. Both the Experimenter and DRDT were notified of this accident. Since the pin could not be run through the profilometer, it was agreed that micrometer measurements be made at 2-inch intervals at 0° and 90° orientations. (The experimenter did not expect too much diameter increase on this low-burnup experiment.) Documentary photographs were taken of the bent pin and will be forwarded to the Experimenter. The other examinations, viz., fission gas sampling, radiography, and gamma scanning will be carried out, with the latter two being performed after the 6-1/2-inch gas plenum section is removed in the inert disassembly box.

Nuclear Materials and Equipment Corporation. The nondestructive tests on NUMEC-A8 and NUMEC-A10 consisted of 2 gross gamma scans and 3 complete spectral scans on each fuel pin.

Microstructural examinations were completed on two additional fuel-clad samples from NUMEC B-11. These examinations included macrophotography, alpha and beta-gamma autoradiography, and optical microscopy.

The shielded microprobe examination of a cross section sample from NUMEC-A10-H was completed.

Material from Other Experimenters. A cask containing ORNL-43-N2, BMI-1-4, BMI-2-5, and LASL-K 37B is scheduled for tentative arrival at LASL about April 16. The nondestructive examinations will begin immediately.

Quality Assurance Program. Rewriting of the Hot Cell and Metallography Standard Operating Procedures to more closely conform to the Quality Assurance requirements was started during this period. The revised versions will then be integrated with the other QA Documents being prepared.

VI. REFERENCES

1. M. M. L. Khosla and S. P. Rao, Talanta, 19, 71 (1952).

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, 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 carbide and nitride fuel assemblies. Contiguous 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. Synthesis and Fabrication

(K. W. R. Johnson, C. Baker, H. Moore, and
R. Walker)

1. Carbide Production

The preparation of pure, single phase $(U_{0.8}Pu_{0.2})C$ fuel for EBR-II irradiation tests was continued. During the course of routine production, radiographic examination indicated one batch of carbide fuel contained pellets which were end-capped. Subsequent batches showed an increasing quantity of end-capped pellets. A complete analysis of each phase of the carbide preparation procedure indicated that the end-capping phenomenon was primarily due to the gradual deterioration of the pressing dies. New replacement dies were ordered.

The nitride fuel pellets for the initial loading of the LASL Series 4 carbide-nitride EBR-II subassembly are to be prepared by Battelle Memorial Institute, Columbus. These pellets are to be supplied with full quality assurance documentation with the exception of final chemical characterization which will be done at LASL. The first of approximately thirteen batches of nitride fuel pellets has been received from BMI, but the material has not yet been unpackaged for inspection.

A quality assurance program is being developed which will be applied to all fuel synthesis and fabrication activities required for the preparation of irradiation experiments. Process procedures, material specifications, data sheets and other quality assurance documents are being prepared, and the management of the fuel preparation operation is being modified as necessary to conform to the requirements of the overall quality assurance plan.

2. Equipment Development

The high temperature tungsten mesh sintering furnace facility was completed. Glovebox and furnace window temperature corrections were measured and incorporated into furnace temperature readings. A 1/8 in. diameter hole, punched in the side of each sintering crucible serves as a black body hole for temperature measurements. To provide the furnace with a pure Ar atmosphere, either flowing or static, a U chip furnace operating at 700°C was incorporated into the system. The inert atmosphere glovebox housing the furnace operates routinely at < 3 ppmO_2 and < 1.5 ppm H_2O.

Several of the carbide preparation procedures require an atmosphere of pure Ar. This has been achieved by passing tank Ar over heated U turnings in a tube furnace. Where such a furnace is used continually, the surface of the U turnings tends to passivate requiring recharging every two weeks. A tube furnace was packed with Ti springs and heated to 900°C in flowing Ar. The Ar flow was periodically monitored for O_2 and H_2O and a purification equal to or superior to U chips was indicated. After 1 month of continuous Ar flow the Ti charge was examined and found to show reaction at the inlet end only. The furnace has now operated continuously for over two months with no indication of Ar purity degradation.

The new H_2 treatment facility is complete except for installation of an outside, all-weather enclosure for the H_2 purification unit. This unit was installed outside to avoid routing high pressure H_2 lines inside the laboratory building. Preliminary heating cycles were made in flowing Ar to test the other components of the apparatus. Only minor modifications were found to be necessary.

As in the H_2 treatment facility, the nitride preparation facility incorporates a H_2 purification unit. Aside from installation of this unit in an all-weather enclosure, the nitride preparation facility installation is complete. Equipment tests will be initiated in the near future.

Work was begun on installation of a high-temperature tungsten mesh nitride sintering furnace in an inert atmosphere glovebox.

A power controller is being modified to provide programmed temperature cycles for the tungsten-mesh carbide sintering furnace.

3. Process Development

Studies were continued to determine the effects of process variables on carbide pellets. Experiments in the new tungsten mesh sintering furnace demonstrated that:

a. In a static Ar atmosphere significant quantities of sesquicarbide form (to 30 vol.%).

b. Pellets heated to 1200°C in vacuum form second phase, probably sesquicarbide.

c. Pellets degassed in vacuum to 700°C then sintered in a stagnant atmosphere are single phase.

d. It is possible to sinter pellets in flowing Ar at 1900°C. No second phase forms.

e. The sintering temperature is a major factor in controlling the final pellet density.

Pressing variables are currently under investigation.

B. EBR-II Irradiation Testing

(J. O. Barner, L. L. Marriott, H. E. Strohm)

The purpose of the EBR-II irradiations is the evaluation of high performance fuel element systems for application in advanced LMFBR reactors. Over the last few years, in addition to the Los Alamos Scientific Laboratory (LASL), Gulf United Nuclear Fuels Corporation (GUNFC), Battelle Memorial Institute (BMI), and Oak Ridge National Laboratory (ORNL) have had development programs concerned with the irradiation of advanced fuels. Presently, all of these programs are being consolidated at LASL. The responsibility for experiments designed by GUNFC that are currently in EBR-II or are partially evaluated has been transferred to LASL. A similar transfer of responsibility for BMI and ORNL experiments is currently in progress. The status of experiments originated by GUNFC and of experiments originated by LASL is included in this report. The status of experiments originated by BMI and ORNL will be reported in future LASL status reports as the responsibility for these programs is transferred.

Four series of LASL-originated experiments are planned. The status of the three series for which approval-in-principle has been received from the AEC is described in Table 463-I. All these experiments use encapsulated fuel elements.

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. The tentative description for these experiments is shown in Table 463-II. The test variables include fuel type, cladding cold-work, smear density, heating rate, operating temperature, and burnup. The fuel used in the fabrication of these elements will be 95% dense, single-phase $(U_{0.8}Pu_{0.2})C$ or $(U_{0.8}Pu_{0.2})N$. The carbide fuel will be fabricated from material synthesized using both arc-melting and carbothermic reduction processes. The nitride fuel for the initial loading will be supplied by Battelle Memorial Institute and will be prepared using the hydride-nitride process. The cladding tubing will be Type 316 stainless steel 0.310 in. O. D. with 0.012 in. walls. The cladding for the tests has been ordered through HEDL from Superior Tube Co. Delivery is behind schedule, but it is anticipated in mid-April, 1972. The cladding will comply, as nearly as is currently available, to the fuel element cladding specification RDT-E-13-8T. End plug material has also been ordered from HEDL. The RDT specification, RDT-M-7-23T, is being used to procure the bar stock for the end plugs. Hold-down springs will be made from the 0.031-in. dia. Type 302 stainless steel FFTF driver fuel element spacer wire material. Final design of this subassembly is awaiting approval-in-principle from the AEC and data for the new EBR-II configuration with the stainless steel reflector.

One of the primary purposes of the Series 4 subassembly is to provide data for a critical comparison of the overall irradiation behavior of carbide and nitride fuel elements which have been irradiated under conditions that are, as nearly as possible, identical.

The status of the experiments originated by GUNFC, for which responsibility has been transferred, is summarized in Table 463-III, IV, V, and VI. A total of 42 elements are either in EBR-II or available for insertion. Eleven elements are in the process of destructive examination.

The 19 fuel elements from Task 5100 as well as capsules U260, U261, and U262 are at LASL for preirradiation examination consisting of non-destructive assay, profilometry, and radiography.

A considerable effort was expended during the quarter in preparing a quality assurance program for fuel element fabrication. Tentative material specifications, operating procedures, data forms, and records files have been prepared and are being reviewed. A quality assurance plan is being prepared for fuel element fabrication for the Series 4 experiments.

C. TREAT Irradiation Testing

(J. F. Kerrisk, 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

TABLE 463-I

SERIES 1, 2, AND 3 EXPERIMENTS[a]

Experiment No.	Series No.	Fuel Type[b]	Fuel Density, % T. D.	Diametral Gap, in.	Max. Fuel Temp. at Startup, °C	Max. Linear Power, kw/ft.	Current Burnup,[a] /o	Subassembly Status
K-36B	1	$(U_{0.8}Pu_{0.2})C$	90	0.015	1165	30	4.0	X142 - In.
K-37B	1	$(U_{0.8}Pu_{0.2})C$	90	0.015	1165	30	3.2	In route to LASL[c]
K-38B	1	$(U_{0.8}Pu_{0.2})C$	90	0.015	1165	30	3.2	X152 - In[d]
K-39B	1	$(U_{0.8}Pu_{0.2})C$	90	0.015	1165	30	3.2	X152 - In
K-40B	1	$(U_{0.8}Pu_{0.2})C$	95	0.020	1150	30	---	To be built
K-41B	1	$(U_{0.8}Pu_{0.2})C$	95	0.020	1150	30	---	To be built
K-42B	1	$(U_{0.8}Pu_{0.2})C$	90	0.015	1165	30	5.0	Completed[f]
K-43	3	$(U_{0.8}Pu_{0.2})C$	95	0.020	1150	30	3.1	X152 - In
K-44	3	$(U_{0.8}Pu_{0.2})C$	95	0.020	1150	30	3.1	X152 - In
K-45	3	$(U_{0.8}Pu_{0.2})C$	95	0.020	1150	30	2.3	X119A - Interim exam
K-46	3	$(U_{0.8}Pu_{0.2})C$	95	0.020	1150	30	2.3	X119A - Interim exam
K-47	3	$(U_{0.8}Pu_{0.2})C$	95	0.020	1150	30	---	To be built
K-48	3	$(U_{0.8}Pu_{0.2})C$	95	0.020	1150	30	---	To be built
K-49	2	$(U_{0.8}Pu_{0.2})C$	95	0.020	1400	45 - 50	3.1	Awaiting shipment to LASL[e]
K-50	2	$(U_{0.8}Pu_{0.2})C$	95	0.020	1400	45 - 50	3.1	X119A - Interim exam
K-51	2	$(U_{0.8}Pu_{0.2})C$	95	0.020	1400	45 - 50	3.1	X119A - Interim exam

a. All elements are clad in 0.300 in. o.d. x 0.280 in. i.d. Type 316SS. All are sodium bonded elements.
b. The Series 1 and 3 experiments are fully enriched in ^{235}U. The series 2 experiments contain 97% ^{235}U. All fuel is single-phase.
c. Capsule K-37B was damaged during reconstitution of X152 to such an extent that it can not be irradiated further.
d. Capsule K-38B was damaged during reconstitution of X152 at EBR-II. Further irradiation is planned.
e. Capsule K-49 will be destructively examined at the request of the EBR-II Project.
f. Reported in LA-4669MS.

TABLE 463-II

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	5	38.3	12.0 (105,000)	1167 (631)	1994 (1090)
1B	3	38.3	12.3 (107,400)	1157 (625)	1975 (1079)
2A	2	38.9	11.7 (102,500)	1060 (571)	1977 (1080)
3A	2	38.8	11.7 (102,400)	1167 (631)	2448 (1342)
3B	3	39.44	11.7 (102,600)	1151 (635)	2486 (1369)
4A	2	39.9	11.4 (100,000)	1078 (581)	2493 (1367)
4B	2	38.8	11.1 (97,200)	1069 (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.

TABLE 463-III

TASK 1300

EBR-II IRRADIATION EXPERIMENTS

Experiment No	Fuel Type[a]	Fuel Density % T.D.	Clad Material	Clad Thickness, in.	Diametral Gap, in.	Fuel-to-Clad Bond	Max. Fuel Temp. at Startup, °C	Max. Linear Power, kw/ft	Current Burnup, (MWD/MT)	Subassembly Status
U93	$MC + 5\ ^{v}/o\ M_2C_3$	84	316SS	0.030	0.004	He	1750	18.0	69,000	X142 - in.
U94	$MC + 5\ ^{v}/o\ M_2C_3$	84	316SS	0.015	0.007	He	1680	21.9	84,000	X142 - in.
U97	$MC + 5\ ^{v}/o\ M_2C_3$	84	INC-800	0.030	0.004	He	1750	18.0	69,000	X142 - in.
U98	$MC + 5\ ^{v}/o\ M_2C_3$	84	INC-800	0.015	0.007	He	1680	21.9	84,000	X142 - in.
U105	$MC + 5\ ^{v}/o\ M_2C_3$	84	INC-800	0.030	0.008	He	1900	15.1	58,000	X142 - in.
U106	$MC + 5\ ^{v}/o\ M_2C_3$	84	INC-800	0.015	0.009	He	1825	19.8	76,000	X142 - in.
U110	$MC + 10\ ^{v}/o\ M_2C_3$	99[b]	INC-800	0.015	0.014	He	1960	21.9	84,000	X142 - in.
U113	$MC + 10\ ^{v}/o\ M_2C_3$	99[b]	INC-800	0.030	0.010	He	1880	16.9	65,000	X142 - in.
U114	$MC + 10\ ^{v}/o\ M_2C_3$	99[b]	INC-800	0.015	0.007	He	1575	22.1	85,000	X142 - in.

a. $M = (U_{0.85}Pu_{0.15})$

b. Cored pellet with nominal 0.080 in. diameter axial hole.

TABLE 463-IV

TASK 1950

EBR-II IRRADIATION EXPERIMENTS

Experiment No.	Fuel Type[a]	Fuel Density % T.D.	Clad Material	Clad Thickness, in.	Diametral Gap, in.	Fuel-to-Clad Bond	Max. Fuel Temp. at Startup, °C	Max. Linear Power, kw/ft	Current Burnup, (MWD/MT)	Subassembly Status
U129	$MC + 5\ ^{v}/o\ M_2C_3$	84	316SS	0.022	0.016	He	1755	12.8	55,000	X055A - in.
U130	$MC + 5\ ^{v}/o\ M_2C_3$	75	316SS	0.022	0.010	He	1500	13.1	56,000	X055A - in.
U131	$MC + 5\ ^{v}/o\ M_2C_3$	84	316SS	0.022	0.010	He	1495	13.1	56,000	X055A - in.
U132	$MC + 5\ ^{v}/o\ M_2C_3$	84	316SS	0.022	0.010	He	1495	12.8	55,000	X055A - in.
U133	$MC + 5\ ^{v}/o\ M_2C_3$	84	316SS	0.022	0.010	He	1495	12.9	55,000	X055A - in.
U134	$MC + 5\ ^{v}/o\ M_2C_3$	84	316SS	0.022	0.010	He	1495	12.8	55,000	X055A - in.
U135	$MC + 5\ ^{v}/o\ M_2C_3$	84	INC-800	0.022	0.010	He	1475	12.8	55,000	X055A - in.
U136	$MC + 5\ ^{v}/o\ M_2C_3$	84	INC-800	0.022	0.010	He	1475	13.3	57,000	X055A - in.
U137	$MC + 10\ ^{v}/o\ M_2C_3$	99	316SS	0.022	0.010	He	1440	13.4	57,000	X055A - in.
U138[b]	$MC + 10\ ^{v}/o\ M_2C_3$	99	316SS	0.022	0.010	He	1440	14.8	18,000	X055A - in.
U139	$MC + 10\ ^{v}/o\ M_2C_3$	99	INC-800	0.022	0.010	He	1440	14.8	63,000	X055A - in.
U140	MC	93	INC-800	0.022	0.010	He	1460	13.9	59,000	X055A - in.
U141	MC	93	316SS	0.022	0.010	He	1460	14.3	61,000	X055A - in.
U142	MC	93	316SS	0.022	0.010	He	1460	14.5	62,000	X055A - in.
U143	$MC + 10\ ^{v}/o\ M_2C_3$	99[c]	INC-800	0.022	0.010	He	1395	12.8	55,000	X055A - in.
U144	$MC + 10\ ^{v}/o\ M_2C_3$	99[c]	316SS	0.022	0.010	He	1395	13.1	56,000	X055A - in.
U145	MC	93	304SS	0.015	0.030	Na	820	13.4	57,000	X055A - in.
U146[b]	$MC + 10\ ^{v}/o\ M_2C_3$	99	304SS	0.015	0.030	Na	810	13.7	13,000	X055A - in.
U147	$MC + 10\ ^{v}/o\ M_2C_3$	99	INC-800	0.015	0.030	Na	810	14.2	60,000	X055A - in.

a. $M = (U_{0.85}Pu_{0.15})$

b. Capsules 138 and 146 were removed at 45,000 MWD/MT for TREAT testing. Duplicates replaced the originals.

c. Pellets cored with nominal 0.080 in. diameter axial hole.

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.

Series UL Tests

A cooperative effort has been initiated with Gulf United Nuclear Fuels Corporation in the area of TREAT testing. A series of four tests, designated LASL

TABLE 463-V

TASKS 1930 and 1960

EBR-II IRRADIATION EXPERIMENTS

Experiment No.	Fuel Type[a]	Fuel Density % T.D.	Clad Material	Clad Thickness, in.	Diametral Gap, in.	Fuel-to-Clad Bond	Max. Fuel Temp. at Startup, °C	Max. Linear Power, kw/ft	Current Burnup, (MWD/MT)	Subassembly Status
U187	MC + 5 $^{v}/_{o}$ M_2C_3	84	316SS	0.020	0.007	He	1935	30.0	45,000	Destructive Exam[c]
U189	MC + 5 $^{v}/_{o}$ M_2C_3	84	INC-800	0.020	0.007	He	1935	30.0	45,000	Destructive Exam[c]
U191	MC	93	304SS	0.015	0.030	Na	1146	31.7	47,000	Destructive Exam[c]
U192	MC	93	304SS	0.015	0.030	Na	1148	31.7	47,000	Destructive Exam[c]
U194	MC + 10 $^{v}/_{o}$ M_2C_3	97	304SS	0.015	0.030	Na	1132	33.1	50,000	Destructive Exam[c]
U195	MC + 10 $^{v}/_{o}$ M_2C_3	97	304SS	0.015	0.030	Na	1132	33.1	50,000	Destructive Exam[c]
U197	MC + 10 $^{v}/_{o}$ M_2C_3	97	INC-800	0.015	0.030	Na	1132	33.4	50,000	Destructive Exam[c]
U198	MC + 10 $^{v}/_{o}$ M_2C_3	97	INC-800	0.015	0.030	Na	1132	33.4	50,000	Destructive Exam[c]
U200	MC + 5 $^{v}/_{o}$ M_2C_3	84	304SS	0.015	0.008	He	2042	30.8	46,000	Destructive Exam[c]
U206	MC + 5 $^{v}/_{o}$ M_2C_3	90	316SS	0.020	0.008	He	2084	31.5	47,000	Destructive Exam[c]
U208	MC + 10 $^{v}/_{o}$ M_2C_3	97[b]	316SS	0.020	0.009	He	1912	31.9	48,000	Destructive Exam[c]
U188	MC + 5 $^{v}/_{o}$ M_2C_3	84	316SS	0.020	0.007	He	1935	30.0	45,000	X152 - in. Awaiting Insertion
U190	MC + 5 $^{v}/_{o}$ M_2C_3	84	INC-800	0.020	0.007	He	1935	30.0	45,000	X119A
U193	MC	93	304SS	0.015	0.030	Na	1148	31.7	47,000	X152 - in.
U196	MC + 10 $^{v}/_{o}$ M_2C_3	97	304SS	0.015	0.030	Na	1132	32.6	49,000	X152 - in.
U199	MC + 10 $^{v}/_{o}$ M_2C_3	97	INC-800	0.015	0.030	Na	1132	33.5	50,000	Interim
U201	MC + 5 $^{v}/_{o}$ M_2C_3	84	304SS	0.015	0.008	He	2042	30.0	45,000	Interim
U207	MC + 5 $^{v}/_{o}$ M_2C_3	90	316SS	0.020	0.008	He	2088	31.7	47,000	Interim
U209	MC + 10 $^{v}/_{o}$ M_2C_3	97[b]	316SS	0.020	0.009	He	1909	30.9	46,000	Interim
U185	MC + 10 $^{v}/_{o}$ M_2C_3	96	316SS	0.020	0.011	He	2195	30.0	< 5,000	X142 - in.
U186	MC + 10 $^{v}/_{o}$ M_2C_3	96	316SS	0.020	0.011	He	2195	30.0	< 5,000	X142 - in.
U202	MC + 5 $^{v}/_{o}$ M_2C_3	84	316SS	0.010	zero	He	1270	31.7	< 5,000	X142 - in.
U203	MC + 5 $^{v}/_{o}$ M_2C_3	84	316SS	0.020	zero	He	1260	31.4	5,000	X142 - in.
U204	MC + 10 $^{v}/_{o}$ M_2C_3	97[b]	316SS	0.010	zero	He	1131	32.2	< 5,000	X142 - in.
U205	MC + 10 $^{v}/_{o}$ M_2C_3	97[b]	316SS	0.020	zero	He	1124	31.9	< 5,000	X142 - in.
U260	MC + 10 $^{v}/_{o}$ M_2C_3	98	316[d]	0.015	0.015	He	2590	34.1	------	At LASL for
U261	MC + 10 $^{v}/_{o}$ M_2C_3	98	316[e]	0.015	0.015	He	2590	34.1	------	Preirradiation
U262	MC + 10 $^{v}/_{o}$ M_2C_3	98	INC-800	0.015	0.015	He	2590	34.1	------	Examination

a. $M = (U_{0.85}Pu_{0.15})$

b. Cored pellets with nominal 0.040 in diameter axial hole.

c. Neutron radiography, x-radiography, and de-encapsulation complete. Elements 194, 200, and 208 had failed.

d. 20% cold-worked.

Series UL, will determine the effect of irradiation on the behavior of helium and sodium bonded advanced fuel elements (fabricated by Gulf United) under possible LMFBR accident conditions. Table 463-VII describes the fuel elements and test objectives. Approval-in-principle has been received from the AEC for this series of tests.

LASL has the responsibility for specifying the TREAT reactor test conditions and preparing the safety analysis required by TREAT for the Series UL tests. Neutronic calculations have been performed to obtain an average energy calibration factor (1.1×10^{-4} MW/cc of fuel per MW of reactor power) and its radial variation in the fuel. The edge to center power generation ratio is 7.6/1. After a consideration of the capabilities of TREAT, it was decided to operate the reactor under computer control for these tests since the maximum power and total energy generated can be controlled more accurately in this mode. Heat transfer calculations, using the calculated energy calibration factor, indicate that a transient generating 70 MW for 1.4 sec, with the associated reactor startup and shut down periods, will achieve the desired results for both He and Na bonded elements. A pre-transient temperature of 260°C (500°F) was chosen. The two unirradiated elements will be tested first.

Calculations for the safety analysis required for these tests have been performed. These calculations

TABLE 463-VI

TASK 5100

EBR-II IRRADIATION EXPERIMENTS

Experiment No.	Fuel Type[a]	Fuel Density, % T.D.	Clad Material[b]	Inner Liner	Diametral Gap, in.	Max. Fuel Temp. at Startup, °C	Max. Linear Power, kw/ft	Status
U241	MC	93	304SS	None	0.015	1175	35.8	At LASL for pre-irradiation examination
U242	MC	93	304SS	None	0.015	1175	35.8	At LASL for pre-irradiation examination
U243	MC	93	304SS	None	0.030	1150	33.8	At LASL for pre-irradiation examination
U244	MC	93	304SS	None	0.015	1175	35.8	At LASL for pre-irradiation examination
U245	MC	93	304SS	None	0.030	1150	33.8	At LASL for pre-irradiation examination
U246	MC	93	316SS	None	0.015	1190	36.4	At LASL for pre-irradiation examination
U247	MC	93	316SS	None	0.030	1150	33.8	At LASL for pre-irradiation examination
U248	MC	93	316SS	None	0.030	1140	36.4	At LASL for pre-irradiation examination
U249	MC	93	INC-800	None	0.015	1210	36.4	At LASL for pre-irradiation examination
U250	MC	93	INC-800	None	0.030	1145	36.4	At LASL for pre-irradiation examination
U251	MC	93	304SS	None	0.030	1145	36.4	At LASL for pre-irradiation examination
U252	MC	93	304SS	Vanadium-slots	0.030	1140	36.4	At LASL for pre-irradiation examination
U253	MC	93	304SS	Iron-slots	0.030	1145	33.8	At LASL for pre-irradiation examination
U254	MC	93	304SS	304SS-slots	0.030	1140	33.8	At LASL for pre-irradiation examination
U255	MC	93	304SS	304SS-holes	0.030	1260	33.8	At LASL for pre-irradiation examination
U256	MC + 10 v/o M_2C_3	98	304SS	Vanadium-slots	0.030	1140	34.0	At LASL for pre-irradiation examination
U257	MC + 10 v/o M_2C_3	98	INC-800	Tantalum-slots	0.030	1135	33.5	At LASL for pre-irradiation examination
U258	MC + 10 v/o M_2C_3	98	304SS	304SS-slots	0.030	1145	33.5	At LASL for pre-irradiation examination
U259	MC + 10 v/o M_2C_3	98	INC-800	304SS-slots	0.030	1150	34.6	At LASL for pre-irradiation examination

a. M = $(U_{0.85}Pu_{0.15})$

b. All elements are sodium bonded. Clad thickness is 0.015 in. for all elements.

included the nuclear effects of the experiment on the TREAT reactor, the nuclear effects of fuel rearrangement, the thermal and mechanical effects of the transient as planned, the thermal and mechanical effects of a larger reactivity addition than planned, and radiation hazards of the experiment. A data package, including the safety analysis, test specifications and a quality assurance plan was submitted for approval.

Series 1 Tests

A group of eight tests using LASL fabricated fuel elements has been designated LASL Series 1 tests. The tests are designed to determine if any significant safety related behavioral problems exist for sodium bonded, stainless steel clad, (U, Pu) C and (U, Pu) N fuels by defining failure thresholds and the types of failure experienced by these fuels. Table 463-VIII summarizes the test parameters and objectives.

Two ORNL TREAT capsules will be modified to incorporate a thermal neutron filter. Without the filter, an edge to center power generation ratio of approximately 10/1 would occur in the fuel. A 0.010 in. thick gadolinium metal filter, located outside the thermal insulation of the TREAT capsule has been selected from preliminary calculations. This choice was based on the following criteria:

TABLE 463-VII

LASL SERIES UL TESTS

	TEST			
	LASL-UL-1	LASL-UL-2	LASL-UL-3	LASL-UL-4
Fuel Element[a]	263 (138 A)	264 (146 A)	265 (138)	266 (146)
Fuel Material[b]	90 vol% $(U_{0.85}Pu_{0.15})C$ + 10 vol% $(U_{0.85}Pu_{0.15})_2C_3$			
Fuel Pellet O. D., in.	0.246	0.240	0.246	0.240
Bond Material	He	Na	He	Na
Bond Thickness (Radial), in.	0.005	0.015	0.005	0.015
Clad Material	316SS	304SS	316SS	304SS
Clad Thickness, in.	0.022	0.015	0.022	0.015
Smear Density, % Theor.	90	77	90	77
Fuel Column Length, in.	---------------- 13.75 ± 0.125 ----------------			
Burnup, MWD/MTM[c]	0	0	45,000	45,000
Test Objective	Fuel Melting	Fuel Melting	Same Transient as 263	Same Transient as 264

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[a] Fuel element numbers reassigned by Gulf United. Old numbers shown in parentheses.

[b] Uranium enriched to 60% in ^{235}U.

[c] Irradiated in EBR-II at 10 - 15 kW/ft in subassembly X-055.

TABLE 463-VIII

LASL SERIES 1 EXPERIMENTS

Test	Fuel Material[a]	Burnup	TREAT Transient[b]	Test Objective
1A-1	$(U_{0.8}Pu_{0.2})C$	0	Fast	Na bond ejection-incipient fuel melting
1A-2	$(U_{0.8}Pu_{0.2})C$	0	Slow	Same as 1A-1
1B-1	$(U_{0.8}Pu_{0.2})C$	0	Fast	50% Fuel melting
1B-2	$(U_{0.8}Pu_{0.2})N$	0	Fast	Same as 1B-1[d]
1B-3	$(U_{0.8}Pu_{0.2})C$	0	Slow	Same as 1B-1
1B-4	$(U_{0.8}Pu_{0.2})N$	0	Slow	Same as 1B-1[d]
1C-1	$(U_{0.8}Pu_{0.2})C$	8%	c	Same as 1B-1
1C-2	$(U_{0.8}Pu_{0.2})N$	8%	c	Same as 1B-1[d]

[a] The fuel will be pellets, contained in 0.310 in. O. D. by 0.012 in. wall 316 stainless steel cladding at 80% smear density. The uranium is enriched to 93% in ^{235}U.

[b] Fast transients will deposit energy in time periods of the order of 1 sec while slow transients will be on the order of 10 sec.

[c] The type of transient to be used will be determined by the results of the unirradiated element tests.

[d] Since (U, Pu) N does not melt, but decomposes to metal and nitrogen, the test objectives are described in terms of the energy required to produce a given melting in (U, Pu) C.

1. the ability to form the filter material into a thin cylindrical shape of uniform thickness which replaces a portion of the thermal insulation of the TREAT capsule;
2. the energy generation in the filter;
3. the melting point of the filter material;
4. the edge to center power generation ratio achieved in the fuel; and
5. the reactivity effect on the TREAT reactor.

The ease of fabricating a Gd metal filter, the high melting point (greater than 1300°C) of Gd, and the low energy generation in the filter from the (n, γ) reaction in Gd were the deciding factors in favor of Gd as the filter material. The choice of thickness was based on a compromise between the resulting edge to center power generation ratio and the reactivity effect of the Gd. The reactivity effect on the reactor of the TREAT capsule with a 0.010 in. Gd filter was calculated to be approximately - 5%, and the edge to center power generation ratio in the fuel was approximately 2/1. A larger negative reactivity insertion was deemed undesirable.[1] More refined calculations are in progress.

A quality assurance program for the Series 1 tests has been initiated. Quality assurance documents covering the experimental plan and the quality assurance requirements for the series are in preparation. Material specifications for the capsule and fuel element components are under review to ascertain the applicability of existing RDT and ASTM specifications. Where no applicable existing specifications were found, e.g. for the fuel and for the thermal neutron filter material, specifications are in preparation. Quality assurance documents covering procedures for fabrication, assembly, and testing of the fuel elements and capsules will be prepared as required in the future.

III. FUEL PROPERTY MEASUREMENTS

A. Differential Thermal Analysis of Irradiated Oxides

(J. G. Reavis, R. Brewer)

The program of differential thermal analysis of the irradiated UO_2-PuO_2 fuel materials supplied by

GE-Sunnyvale is continuing. The accumulated data has been treated statistically to determine the accuracy of determination of thermal arrest temperatures.

Correction of temperatures measured using optical pyrometric techniques was made according to the equation

$$\frac{1}{Tc} = \frac{1}{To} + A$$

where Tc is the corrected temperature in deg. K

To is the observed temperature in deg. K

A is a constant whose value depends on light absorption by the optical system between the furnace and the pyrometer.

A was evaluated by multiple determinations of melting and freezing temperatures of high purity samples of Pt, Rh and Ir standards contained in ThO_2 crucibles. The melting (and freezing) points of Pt, Rh and Ir, as adopted by the International Committee on Weights and Measures, are 1769, 1960 and 2443°C, respectively. Based on a total of 52 observations of melting and freezing of these metals, the value of A was determined to be $(65.03 \pm 0.18) \times 10^{-6}$ at the 95% confidence level. As an example, the uncertainty in this correction is ± 5° at a corrected temperature of 2550°C.

The variances of the corrected temperatures of thermal arrests observed for each sample of UO_2-PuO_2 were then calculated by use of the formula

$$\sigma^2_{T_c} = \frac{\sigma^2_{T_o} + T_o^{-4}\sigma^2_A}{(1 - A T_o)}$$

TABLE 463-IX

THERMAL ARRESTS OBSERVED FOR SAMPLES OF UO_2-PuO_2 IN SEALED TUNGSTEN CAPSULES

Sample	% PuO_2	O/M	No. of Cycles	Burnup, a/o	Arrest Temps. °C	
					Heating	Cooling
A-1	25	1.96	3	0.0	2786 ± 21	2831 ± 18
A-2	20	2.00	3	0.0	2714 ± 27	2782 ± 41
F3B-7C-1	25	1.98	2	4.3	2766 ± 91	2827 ± 46
F3B-7C-2	25	1.98	7	4.3	2732 ± 13	2775 ± 14
F3B-7C (All)	25	1.98	9	4.3	2741 ± 45	2788 ± 58

where σ^2 is the variance. The 95% confidence limits of the values of corrected temperatures of thermal arrests were then calculated from σ for all measurements on each sample.

The average values of arrest temperatures observed for four capsules of UO_2-PuO_2 are listed in Table 463-IX with their 95% confidence intervals. The word "solidus" was not used in Table 463-IX because no physical proof was obtained to show that the thermal arrest observed during heating was at the temperature of first liquid formation. Based on previous observations, no macro melting was encountered at temperatures below the observed arrest, but this does not eliminate the possibility that microscopic inclusions (particularly in the irradiated samples) may have melted at lower temperatures without a detectable thermal arrest. Similarly, the cooling arrests listed in Table 463-IX may not be true liquidus temperatures, but are temperatures of macro freezing of the samples.

With one exception, the confidence levels listed in Table 463-IX are acceptably small. The large uncertainty in the heating arrest temperature listed for sample 1 of F3B-7C is largely due to the small number of observations. When both samples of F3B-7C are considered as one, the uncertainty is also rather large, because of the differences between samples 1 and 2 in addition to the large uncertainty associated with sample 1. While it is possible that there is some chemical difference between the two samples, this seems to be a rather unlikely explanation.

Another unexpected observation in Table 463-IX is the relation of arrest temperatures of samples A-1 and A-2. Based on U/Pu ratios alone,[2] A-2 would be expected to have higher solidus and liquidus temperatures than A-1. Although the difference in O/M ratios might have some effect,[3] the effect is not expected to be this large.

DTA observations on additional capsules of these samples as well as on samples having higher burnup levels are planned, but additional development of dependable welding techniques is needed first. Inspections of capsule welds have revealed problems of limited penetration and cracking of welds because of large grain formation. The effects of welding current, rate of electrode travel, and capsule geometry are being investigated. Although improved welds have been obtained, a technique which insures reproducible crack-free welds has not yet been developed.

B. High Temperature Calorimetry of Irradiated Oxides

(David G. Clifton, R. Brewer)

New determinations of the self-heating of the irradiated sample of $U_{0.8}Pu_{0.2}O_{2.00}$ from NUMEC-B-9 were made. This set of determinations was made about 1 year after the first set of such measurements. The specific power is presently about 3.41×10^{-3} watts/gm as compared with the previously determined value of about 6.21×10^{-3} watts/gm; the ratio of the present to former power is 0.55. This compares very well with an approximate value of 0.61 that can be obtained by interpolation of the energy release from the decay rate curves of fission products as calculated by Perkins and King[4] as a function of reactor operating period and time after shutdown. Utilizing these two measured specific powers and linear interpolation, all data taken on the irradiated sample were corrected for the appropriate change in specific power as a function of time. An additional six data points were taken for the irradiated sample.

The enthalpy measurements reported earlier for the Standard Reference Material 720, synthetic sapphire (Al_2O_3), were compared with the recommended NBS values and found to be low; the cause of this discrepancy has not been found as yet. From a plot of the differences between these two sets of data and from a comparison of a smoothed curve through the observed data with the NBS data curve it is concluded that the values obtained in the hot cell, on the average, are 1.4% lower than the recommended values. Using the NBS values as a reference, this is interpreted as indicating that a systematic error in the data obtained using the hot cell calorimeter as calibrated electrically. The previous hot cell measurements on the mixed oxides should be corrected, therefore, by + 1.4%. This may be considered as a calibration of the calorimeter system using the NBS Al_2O_3 standard. The 1.4% correction has been applied to the NUMEC oxide values, which were based on electrical calibration, and the data are reported in Table 463-X. The data are given in cal/gm for comparative purposes since the molecular weight of the irradiated material is not accurately known. The last column of Table 463-X presents the data for the NUMEC archival material in the units of cal/mole for convenience of comparison with other workers. Graphical comparison of the measurements for the NUMEC archival sample with the recent higher temperature data of Leibowitz, Fisher, and Chasanov[5] and with the earlier work of Ogard and Leary[6] has been made. In general, the data all compare favorably, but some variation is apparent. This may be due to the fact that the data were obtained using three different calorimeter systems, hence comparison of accuracies is difficult, and that there are differences in the composition of the materials. All these data presently are being examined more thoroughly and are being fit to analytical expressions; a more detailed account of this analysis to be given later.

A leak in the cooled outer shell of the furnace in the hot cell calorimeter was found during the acquisition of the last set of data; this is now being repaired.

TABLE 463-X

ENTHALPY MEASUREMENTS

$U_{0.8}Pu_{0.2}O_{2.00}$ Irradiated NUMEC-B-9-56			$U_{0.8}Pu_{0.2}O_{2.00}$ Unirradiated NUMEC Archive			
T°C	T°K	H_T-H_{298} cal/gm	T°C	T°K	H_T-H_{298} cal/gm	H_T-H_{298}[a] cal/mole
1186	1459	87.4	1013	1286	69.9	18734
1321	1594	102.6	1237	1510	91.4	24496
1357	1630	103.0	1340	1613	98.5	26399
1358	1631	102.5	1500	1773	111.3	29830
1463	1736	112.5	1579	1852	120.3	32242
1529	1802	117.8	1712	1985	132.1	35404
1597	1870	125.0	1797	2070	139.5	37387
1611	1884	126.8	1865	2148	149.6	40094
1662	1935	131.1	1958	2231	158.0	42346
1721	1994	136.3	2078	2351	171.8	46044
1810	2083	144.5	2204	2477	180.9	48483
1832	2105	149.5				
1901	2174	152.5				
1954	2227	155.4				
1971	2244	160.9				
1999	2272	132.6				
2024	2297	166.0				
2125	2398	177.7				

[a] Based on a molecular weight of 268.01.

C. UO_2 Heat Content

(J. F. Kerrisk and D. G. Clifton)

A knowledge of the enthalpy or heat capacity of a nuclear fuel is important in the safety analyses of reactors, since these properties are required to relate energy generation in the fuel to the fuel temperature during transient operation. An accurate knowledge of fuel temperatures is necessary to evaluate feedback mechanisms and fuel element behavior. Although the enthalpy of UO_2 has been measured at high temperatures by a number of investigators, no single correlation of enthalpy data is available.

UO_2 enthalpy data, measured by drop calorimetry, has been fit to a theoretically based equation applicable from room temperature to the melting point. A total of 105 data points from five different investigators were used.[7-11] Initially, polynomial and spline functions were fit to the data. Both types of functions provide an adequate fit to the enthalpy-temperature data, but when differentiated to obtain the heat capacity-temperature function, the results were less pleasing. In particular, the heat capacity curve exhibited a maximum near 2800 to 3000 K, decreasing with increasing temperature beyond this point. This phenomenon is not expected for UO_2 at high temperatures. Rather than try to restrict the behavior of empirical functions, a more theoretically based function was sought.

The heat capacity of UO_2 was assumed to be composed of three contributions, (1) a lattice contribution, C_v, (2) an expansion contribution, C_E, and (3) a defect contribution, C_D. The lattice contribution was taken as an Einstein function,

$$C_v\,(T) = \frac{K_1\theta \exp(\theta/T)}{T^2\,[\exp(\theta/T) - 1]^2} \qquad (1)$$

where T is temperature (K), θ is the Einstein temperature, and K_1 is a constant. The expansion contribution was assumed to be proportional to temperature,

$$C_E\,(T) = 2K_2\,T, \qquad (2)$$

where K_2 is a constant. The defect contribution was taken as

$$C_D\,(T) = \frac{K_3 E_D}{RT^2} \exp(-E_D/RT) \qquad (3)$$

where E_D is the energy of formation of a defect, R is the gas constant, and K_3 is a constant.[12,13] The resulting heat capacity is

$$C_p\,(T) = C_v\,(T) + C_E\,(T) + C_D(T). \qquad (4)$$

The enthalpy was obtained as

$$\Delta H\,(T) = \int_{298}^{T} C_p\,(T)\,dT \approx K_1\theta\{[\exp(\theta/T)-1]^{-1} - [\exp(\theta/298)-1]^{-1}\} + K_2\,(T^2 - 298^2) + K_3 \exp(-E_D/RT). \qquad (5)$$

The term due to evaluating the integral of C_D (T) at the lower limit (298 K) was dropped as a simplification in Eq. (5) since its contribution to ΔH (T) was expected to be small. (The actual contribution is less than 10^{-18} cal/mole with the final values of K_3 and E_D.) Equation (5) constrains ΔH (298) to be zero. Since the data that were fit are quite sparse below 700 K, it was felt that fitting Eq. (5) directly would not give a good estimate of C_p (298). This would also ignore data from independent measurements of C_p (T) at low temperatures. For these reasons C_p (298) was fixed for the fit, and the value chosen by the IAEA in 1965 was used; C_p (298) ≡ 15.2 cal/mole K.[14] To accomplish this we have (neglecting $C_D(298)$)

$$C_p\,(298) = \frac{K_1\,\theta^2 \exp(\theta/298)}{(298)^2\,[\exp(\theta/298)-1]^2} + 2\,(298)K_2, \qquad (6)$$

as a relation between the constants K_1, K_2, and θ necessary for the calculated heat capacity at 298 K to be C_p (298).

Equation (5) with the constraint of Eq. (6) was least squares fit to the enthalpy-temperature data. Rather than minimize the sum of squares of the actual deviations (observed-calculated heat constant), the sum of the squares of the percentage deviations was minimized, since it was observed that the percentage deviations were approximately constant over the range of measurements. This is in line with the assumption that

TABLE 463-XI

CONSTANTS IN EQUATION (5)

Constant	Units	Value	Standard Deviation
θ	K	535.285	8.86
E_D	kcal/mole	37.6946	2.39
K_1	cal/mole K	19.1450	----
K_2	cal/mole K^2	7.84733×10^{-4}	1.38×10^{-4}
K_3	cal/mole	5.64373×10^{6}	2.04×10^{5}

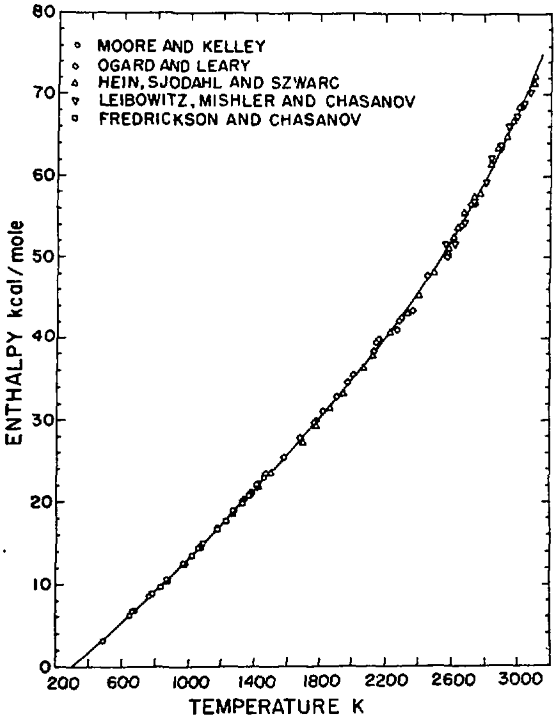

Fig. 463-1. Enthalpy of UO_2 as a function of temperature.

experimentally the percentage error is constant. Table 463-XI shows the final values of the constants obtained. Figure 463-1 shows a plot of the enthalpy data as a function of temperature along with the calculated curve. Figure 463-2 shows a plot of the actual and percentage deviations of the data from the calculated curve. Some systematic differences between various sets of data are

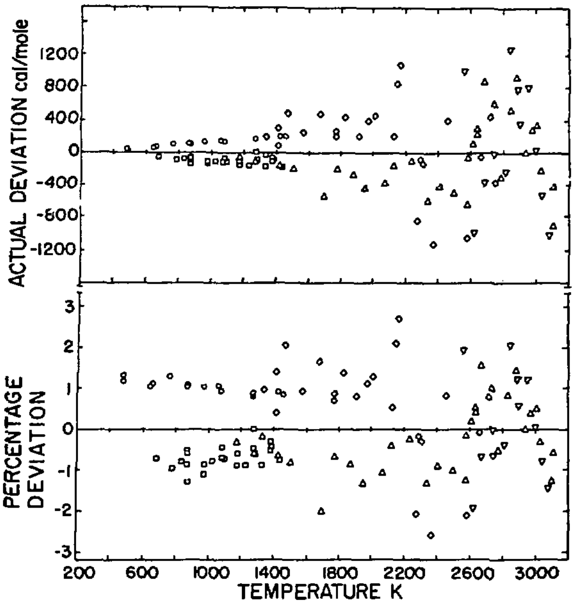

Fig. 463-2. Deviations and percentage deviations of measured enthalpy from calculated curve. Data point legend shown on Fig. 463-1.

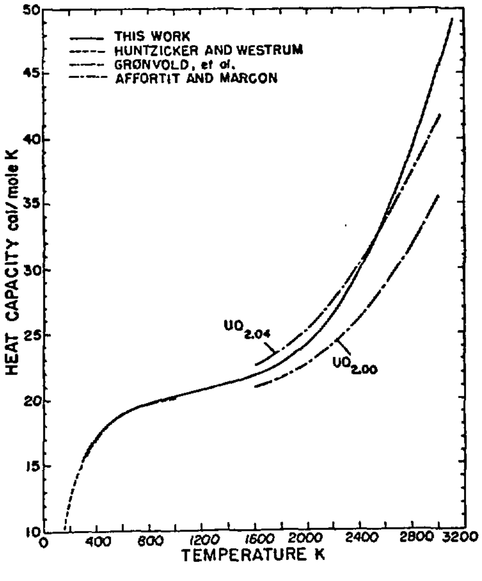

Fig. 463-3. Heat capacity of UO_2 as a function of temperature.

evident from this plot. The maximum deviation of the data from the calculated curve was 2.7%. Figure 463-3 shows a plot of the heat capacity, calculated from Eq. (4), as a function of temperature. In addition, curves of measured heat capacity from three different sources are shown for comparison.[13,15,16] None of these data was used in the least squares fit.

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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 product 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 in 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 post-irradiated 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 under way 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, R. D. Gardner, A. L. Henicksman, W. H. Ashley, C. F. Metz)

The first AEC-Internal Round Robin to evaluate methods for measuring the chemical properties included in the specifications of boron carbide was completed in September 1971.[1] Methods for determining total boron, total carbon, and isotopic boron were judged to be satisfactory. The four methods for determining soluble boron, soluble carbon, chloride and fluoride, and metal impurities were subsequently improved, and a second AEC-Internal Round Robin was conducted to evaluate the improved methods. The round robin samples were a powder blend of boron carbide and added amounts of chloride and fluorite salts for the evaluation of the halogen determination method, and batches of boron carbide pellets (supplied by HEDL) for the evaluation of the other three methods. The round robin results demonstrated that the four improved methods were satisfactory, and, therefore, the first round robin with industry participation is scheduled for the near future. Plans have been formulated for this round robin, and the preparation of the test samples is under way.

Technical highlights of the improvements made in the four methods for measuring the following chemical specifications are given here.

Chloride and Fluoride. In this method, the halogens are separated from a mixture of the sample and U_3O_8 accelerator by pyrohydrolysis in moist gas at elevated temperature. The halogen acids formed by hydrolysis collect in the condensate, and the chloride and fluoride are determined by chemical methods. Since the first round robin, the recovery of halogens in the HEDL tentative method has been improved passing the flow gas through boiling water to increase its water content, and by increasing the reaction temperature to 1000°C. These are conditions used at LASL for this determination.

Soluble Carbon. In this empirical method, a weighed portion of the pulverized sample is reacted with a specified mixture of sodium dichromate-sulfuric acid for a 1-hr period at a designated temperature in the range of 90 to 110°C. It is assumed that only uncombined carbon, but no B_4C, is oxidized to form CO_2 which is collected and manometrically measured.

Use of this method produced large between-laboratory differences which were traced to variations in the reaction heating parameters among the laboratories. Our investigation showed that the amount of CO_2 formed was proportional to the total heat input as well as to the maximum temperature that was reached. By meticulously describing the apparatus and procedural operations to assure equal analysis conditions among laboratories, differences have been reduced to an insignificant level.

Our investigation of this method is being continued to evaluate the reaction of various elemental carbon-boron species with the specified reagent as a function of heating time and temperature (see Section B.1).

Soluble Boron. Soluble boron is measured in the solutions produced by digesting two separate samples under reflux with different acids for 1-hr periods. A digestion with 0.1 N HCl is intended to dissolve boron oxide only; digestion with 1.6 M HNO_3 is intended to dissolve both elemental boron and boron oxide. Modifications by HEDL and LASL in the measurement of boron improved the reliability of the method. The HEDL modification was the removal of interfering impurities on a cation exchange column before the mannitol potentiometric titration for the boron, and LASL developed a flame emission method for this determination.[2]

Present studies at LASL (see B.2) are to determine the boron species that dissolve under the empirical conditions presently used and also in other reagents.

Metal Impurities. Three major modifications in this method greatly improved its reliability. First was the use of a series of calibration blends, prepared at LASL, by all participating laboratories. The other modifications were the use of the same specified analytical lines by all laboratories and the simultaneous processing of samples and calibration blends to permit direct comparison of intensities of spectral lines of samples to those of the calibration materials. These modifications have been described[3] and current studies are discussed in Section B.3.

B. Studies and Improvements of Analytical Methods

1. Determination of Soluble Carbon

(A. L. Henicksman and W. H. Ashley)

Soluble C is measured manometrically as CO_2 following wet oxidation of the pulverized sample in dichromate-sulfuric acid at 100° to 110°C for 1 hr. As stated previously (see Section II.A), the results obtained using this empirical method for soluble C are dependent upon the reaction temperature and the length of the heating. For one lot of B_4C, the measured soluble C content increased from 0.66% at a reaction temperature of 80°C to 0.92% at 105°C, and then at a rapidly increasing rate to 1.28% at 120°C. The difference in the soluble C results measured at the extremes of the recommended temperature range, 100° to 110°C, was about 12%. Either a constant temperature oil bath or an electric heating mantle was satisfactory for heating the solution.

To assure that adequate oxidant was present for quantitative wet oxidation of the C, several samples of B_4C containing about 11% free C were analyzed using the specified quantity of dichromate-sulfuric acid oxidant. Approximately 10 mg of C was oxidized in these samples as compared to 2 mg in most B_4C samples. The results were reproducible and accurate, indicating that the quantity of oxidant was more than adequate for the normal amount of C usually oxidized. Prolonged heating, after an initial period of 3 to 4 hr. of all B_4C materials analyzed to date resulted in a constant rate of increase of dissolved B and oxidized C in amounts corresponding closely to the atom ratio of 4 to 1. These results not only show that there is excess oxidant but also that B_4C is being attacked. For these reasons, it is imperative that analysis conditions be meticulously detailed and followed to obtain reproducible results.

An investigation has been started of the types of C that are oxidized by dichromate-sulfuric acid at various temperatures.

2. Determination of Soluble Boron

(R. D. Gardner, A. L. Henicksman, and W. H. Ashley)

Soluble boron is measured by chemical titration following leaching of the sample with 0.1 M HCl to dissolve B_2O_3 and with 1.6 M HNO_3 to dissolve B_2O_3 and elemental B. No problem exists in analyzing the B dissolved by 0.1 M HCl, but removal of Fe and Al by a cation exchange resin column is necessary before titrating B in the neutralized HNO_3 leach solution. The retention of Fe and Al by the resin was improved by using a resin having a cross linkage of 2 instead of 8. Further improvement in separation was attained using an aliquot of the acid solution without neutralization for the ion exchange treatment and also the titration. The precision of the analyses also was improved, but some difficulties remained in the ion exchange separation. In addition, prolonged refluxing in 1.6 M HNO_3 dissolved B at a continuing significant rate, indicating some attack on B_4C.

Studies of the leaching of B_2O_3 and elemental B with slightly acidified H_2O_2.[4] instead of 1.6 M HNO_3, gave promising results. The cation exchange resin removal of Fe and Al from this solution was without difficulty. In addition, the apparent dissolution of some B_4C by HNO_3 was avoided. Leaching with H_2O_2 acidified with acids other than HNO_3 is being investigated.

3. Emission Spectrographic Determination of Metal Impurities

(O. R. Simi)

In the spectrographic determination of metallic impurities in B_4C, described in HEDL TME-71-54, Method 20.4, the electrode sample, which contains 10% B_4C sample, 22.5% GeO_2, and 67.5% graphite powder, is burned to completion in a d.c. arc, and the spectrum is recorded on S.A.-1 plates. Results are obtained by visual comparison of analytical lines in the sample spectrum with spectra of calibration materials on a previously prepared calibration, or reference, plate. Improvement in the reliability of this method was attained by the following modifications: (1) use of one set of calibration materials to contain all the required elements at concentrations from 0.1 to 4 times the specification limits, (2) exposure of the calibration materials on the same spectrographic plate as samples, (3) use of a grating spectrograph with a reciprocal linear dispersion of 5 Å/mm, (4) use of a center-post electrode, (5) use of B_4C in the calibration materials, (6) specification of the analytical lines to be used for each element, and (7) recommendation of microphotometry for the determination of any impurity element found at greater than 25% of the specification limit.

The precision of the results obtained, following these modifications, was approximately 5%, expressed as relative standard deviation (RSD), from 4 replicates on each of 6 pellets. The precision of the results on a control sample, analyzed twice on each of 3 plates, ranged from 2.5 relative percent for measuring Mn to 9.5 relative percent for Cr.

Calibration materials were prepared for the next round robin (scheduled to begin April 1) to provide 150 mg of each calibration blend for each participating laboratory.

The new calibration materials were tested and were found to produce calibration curves coincident with those from previously used calibration materials.

Work was started on an alternate method of analysis that starts with the fusion of B_4C with Na_2CO_3 and subsequent conversion of the excess Na_2CO_3 to NaCl. Current experiments are directed toward producing a gravimetrically reproducible product.

III. ANALYTICAL CHEMISTRY PROGRAM FOR LMFBR/FFTF FUEL

A. Preparation of an RDT Standard of Methods of Chemical Analysis for FBR Uranium-Plutonium Oxide Fuel and Source Materials

(J. E. Rein, G. M. Matlack, R. T. Phelps, G. R. Waterbury, C. F. Metz)

This RDT Standard is being prepared as a joint HEDL-LASL effort. The more than 25 methods to be included in this document have been selected on the basis of highest reliability and lowest cost in both equipment and manpower effort. The first draft of the document has been completed and final revision is under way.

B. Development of Fuel Burnup Measurement Methods

(R. M. Abernathey, J. E. Rein)

In cooperation with the Allied Chemical Corporation (Idaho Falls, Idaho) and the Argonne National Laboratory, a document is being prepared which presents the status of burnup measurements for FBRs with an emphasis on chemical methods. Final typing of this document has been started.

The last report[5] described modifications in the sequential separation[6] for obtaining plutonium, uranium, and neodymium fractions from irradiated fuels. One modification was the use of commercial, disposable plastic columns, rather than custom-fabricated glass columns, to decrease costs and minimize cross contamination. Other improvements are being planned.

IV. REFERENCES

1. "Quarterly Status Report on the Advanced Plutonium Fuels Program, July 1 to September 30, 1971," LA-4841-MS, Los Alamos Scientific Laboratory (1971), pp. 15-16.
2. "Quarterly Status Report on the Advanced Plutonium Fuels Program, October 1 to December 31, 1971," LA-4913-PR, Los Alamos Scientific Laboratory (1971), p. 22.
3. Ibid, pp. 21-22.
4. E. E. Kotlyar, T. N. Nazarchuk, Zh. Anal. Khim., 15, 207 (1960).
5. Ibid, pp. 25-26.
6. "Sequential Ion Exchange Separation and Mass Spectrometric Determination of ^{148}Nd, Uranium, and Plutonium in Mixed Oxide Fuels for Burnup and Isotopic Distribution Measurements," R. M. Abernathey, G. M. Matlack, J. E. Rein. Presented at the "Symposium on the Analytical Chemistry of the Nuclear Fuel Cycle," IAEA, Vienna, November 28-December 2, 1971.