LA-5067-PR

PROGRESS REPORT

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Quarterly Progress Report on the

Advanced Plutonium Fuels Program

April 1 to June 30, 1972

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

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This report presents the status of the LASL Advanced Plutonium Fuels program. The four most recent reports in this series, all unclassified, are:

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Compiled by

R. D. Baker

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

TABLE OF CONTENTS

ABSTRACT

This is the sixth annual report on the Advanced Plutonium Fuels Program conducted at the Los Alamos Scientific Laboratory. Results of the current quarter's work has been in most cases incorporated into the summary of the year's work, and is therefore specifically identified.

Most of the investigations discussed 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 the report should not be made without obtaining explicit permission to do so from the persons in charge of the work.

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

(M. E. Lazarus, D. C. Maestas, P. A. Mason, E. O. Quintana, R. F. Velkinburg)

1. Disassembly Cell. The inert atmosphere of the cell was maintained throughout FY 1972 by a recirculating gas purification system. Concentrations of < 10 ppm O_2 and < 2 ppm H_2O were consistently maintained, with many weeks of < 5 ppm O_2 being achieved. There has been a gradual increase in the typical H_2O concentration beginning in January 1972, from < 2 ppm to approximately 5 ppm. Various experiments and consultation with the purifier manufacturer representatives indicate there is probably a gradual deterioration of the molecular sieve material in the purifier. Replacement of the adsorbent is planned should routine readings approaching 10 ppm be observed.

A new recirculating gas purification system has been received. Specifications for this unit and the arrangement of the accessories are designed to permit sufficient mobility for attaching the unit, with short notice, to either the disassembly cell or other hot cells within the complex.

2. Metallography Cells. The inert atmospheres of these two cells and the metallograph blister were maintained throughout most of the 1972 FY by a once-through argon purge. Return to the use of a recirculating gas purification system for these cells has been postponed

pending the installation of a refrigerated butyl acetate removal system. The acetate and other solvents used in the cells have caused rapid deterioration in the performance of the purifier.

The experimental PVC manipulator boots, with a polyurethane exterior coating, proved to be considerably more resistant to the deteriorating effects of the solvent vapors than the previous all-PVC boots. The coated boots were still in good condition after seven months exposure, compared to a four-month average life for the all-PVC boots.

Diffusion of air through boots exposed to high levels of solvent vapors continued to be a problem. Sealed tube, Model "L" manipulators were installed in the polishing and etching cell in May 1971. Experience indicated that, although the air leak rate was significantly reduced, the manipulators were not capable of handling the higher mechanical work loads required in the adjoining grinding cell without some in-cell equipment modifications. These modifications were made and the Model "L" manipulators were recently installed in the cell. Modified manipulator adapter sleeves with an improved seal were also installed in both cells.

A special shroud, fabricated of PVC film, was designed to enclose the remotized Bausch and Lomb metallograph and permit a slight pressurization with Ar to prevent contamination of the unit while the specimen mount port was open to the new blister interior. The mount support and plug assembly were modified to improve the seal and ease of operation. The new blister assembly has a lower air leak rate than the previous assembly.

B. New Metallograph Compartment

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

A new metallograph compartment was installed in place of the existing unit attached to the metallography cell culminating several months of design, fabrication, set-up and checkout.

The new compartment can accommodate two metallographs (the original Bausch and Lomb instrument plus a new remotized Leitz metallograph) to increase the throughput capability. In addition an Ion Etcher capability has been built into the box for activation at a later date.

The compartment incorporates several new features which include:

1. A pair of PaR True Motion Mini-Manipulators for better coverage and operating capability within the containment box.
2. A specially designed gate valve operated by the manipulators for the transfer system to the polishing cell.
3. A new design in a bag-out port incorporating a sealed telescoping mechanism and a vault type shield door.
4. A special bolt-down hatch, sealed by means of a gasket, in the top for ease of access in possible future changes including the ion etcher equipment which has not yet been completely defined.

Since this box utilizes an inert Ar atmosphere, an extensive effort was made to eliminate leaks. A substantial leak through the drive train for the transfer mechanism (previously existing) was discovered and eliminated.

Service engineers checked out both metallographs for proper alignment and response prior to the final installation. The complex has now been in use nearly 2 months and is performing as planned.

C. Fuel Pin Handling System for Betatron Radiography

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

A vertical transport device for removing a fuel pin (up to 61 in. in length) from the radiography cask (see item D below), handling for radiographic exposures, and replacing the pin in the cask has been designed and is being fabricated. This improved mechanism will allow a remotely adjustable and incremental method of raising the pin in a precise manner.

The mechanism is mounted on three wheels and can be rolled manually and attached to the cask to provide the stability required. From this point on, the attachment to the pin and all other motions, including a 90° rotation to provide radiographs at 0° and 90°, are accomplished by remote control behind a shielding wall.

D. Radiography Cask

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

A new radiography cask has been designed for handling fuel pins up to 61 in. long and with burnups as high as 10%. Depleted uranium is used for shielding; additional shielding is provided over the center portion of the cask where the fueled section of the pin is located.

The design was made in accordance with the Department of Transportation requirements. Approval of a Special Permit is in process.

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 October 1972.

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

E. Shipping Cask

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

A small 1500 lb cask (DOT-SP-6421), designed to ship short sealed sections of fuel pins off-site, was received in February. This cask was made available in June to the Sandia Corporation and the University of New Mexico for transferring ^{60}Co "pencils".

A third 22-ton "Rover Type" cask was received, and modifications were accomplished in the lid and lid fasteners (special nuts) to ensure an adequate seal for shipping.

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

Three boron-poisoned inserts have been designed and fabricated. Each insert is capable of holding up to 12 unencapsulated pins (61 in. in length). Up to three inserts can be shipped in a Rover cask at one time.

F. Cask Insert Elevator

(J. M. Ledbetter, C. D. Montgomery, T. Romanik, R. F. Velkinburg)

A remotely operated, 200 lb capacity, electromechanical elevator for use inside the Rover type casks was designed, fabricated, and tested. This device permits proper loading and unloading of these casks by remote operation, and it has provided positive, safe control. Another unit is now being made for the second Rover cask used primarily for storage. (See Fig. 401-1.)

G. Butyl Acetate Removal System

(G. S. Dow, M. E. Lazarus, P. A. Mason)

A refrigeration cold trap unit for removing butyl acetate (used as a grinding vehicle and fluid in the ultrasonic cleaners) has been designed. It will be installed in the inert gas recirculating purifier system to provide improved atmospheres for the metallography cells.

H. Improved Alpha Box Design

(F. J. Fitzgibbon, P. A. Mason, C. D. Montgomery, J. R. Trujillo)

The alpha box design has been revised with several improvements including: the capability for remotely replacing the periscope window; relocated glove ports for ease of operation; modified manipulator and light wellports for additional lateral adjustment capability; and relocated 7-Inch Transfer System. An order for two of these assemblies has been processed. Delivery is scheduled for September 1972. Preliminary design for a chilled water radiator assembly for control of the temperature of the alpha box atmosphere has been completed which will be compatible with the new boxes.

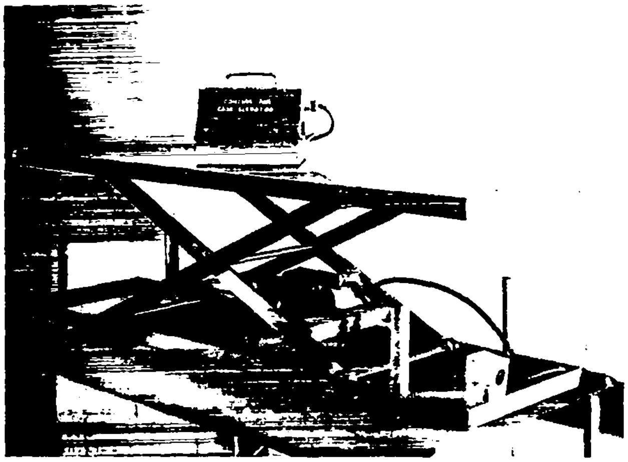

Fig. 401-1. Elevating Mechanism for Rover Cask

I. Manipulator Maintenance Program

(J. M. Ledbetter, P. A. Mason, E. L. Mills)

A program of complete overhaul of the master-slave manipulators for the Wing 9 and DP West Facilities was initiated in February. Sixteen manipulators were completed by the end of the report period, requiring approximately 40 manhours each. Ten technicians have been involved in the program sufficiently to perform overhaul or repair work with some supervision. One technician is presently being trained to perform the overhaul, repair, and general maintenance work on the various types and models of manipulators with a minimum of supervision.

J. Venting Device for Shield Plugs

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

During March 1972, it was pointed out that the sealed 10-in.-diameter, 32-in.-long shield plugs in the Wing 9 Facility may contain pressurized hydrogen due to a chemical reaction of moisture and the packed ferro-phosphorous aggregate inside. Moisture may have been in the plug containers at the time the lid was attached by welding.

A special drill type puncturing device was designed and fabricated to permit safe removal of this hydrogen. This device permitted evacuation of the drilling tool by means of a vacuum pump prior to puncturing, total containment, and controlled bleed-off of H_2 following the puncture.

This system was used to puncture some forty-four plugs and dispose of the H_2. The highest pressure observed was approximately 360 psi while some plugs indicated only atmospheric pressure when punctured.

K. In-Cell Equipment

(G. R. Brewer, E. L. Ekberg, F. J. Fitzgibbon,
D. D. Jeffries, M. E. Lazarus, P. A. Mason,
C. D. Montgomery, T. Romanik, J. R. Trujillo)

1. Optical Gauge for Diameter Measurement. A new design for modification of the Bausch and Lomb DR2SB Optical Gauge has been completed and submitted to the shops where fabrication is approximately 75% complete. This design incorporates a system for adjusting the position of even a severely bowed fuel element so that the axis is perpendicular to the measuring anvils at the point of measurement. This gauge will supplement the existing profilometry equipment.

2. Fuel Element Length Gauge. A fuel element length gauge has been designed and built to measure the length of straight fuel elements. Slightly bowed fuel elements can be measured by placing them in one of the holding-straightening fixtures. The gauge accommodates an element up to 62 in. in length and can be read to ± 0.0001 in. The claimed accuracy in ± 0.001 in. which can be improved, if necessary, by accurately measuring gauge and fuel element temperatures at every inch along the length; the appropriate corrections are then applied to correct for the temperature.

3. Mechanical Profilometer. A preliminary design has been completed on a new mechanical profilometer. This unit will be an improvement on the profilometer now in the disassembly cell. It will have a sturdier frame, and the LVDTs will be easier to replace than those on the present unit. It also will correct for the errors that fuel element bow introduces in profilometry measurements by insuring that the sensors are always perpendicular to the fuel element at the point of measurement. When completed, it will replace the unit now in the disassembly cell.

Several new types of profilometer probes were designed, built, and tested in use to optimize the response and reliability of the mechanical profilometer currently being used. The best design is apparently a probe using 304 stainless steel for the main body, since ferrous material cannot be used at this location, and using a 440 stainless steel hardened tip with a chrome plating to minimize contact friction with the fuel pin during the scan. Further testing is needed to prove total compatibility of the system.

4. Hi-Pressure Potting of Metallographic Samples. Modifications were made to a commercially procured high-pressure vessel to adapt it for remote use in the metallography alpha box.

With the use of high-pressure stainless-steel plumbing, a proper safety and control system, an overhead hoist (internal to box), a vacuum pump-down system, and an Ar pressurizing supply, the system was tested and installed. The system is presently using normal Ar bottle pressures of 2000 + psi. Pressures up to 4000 psi could be used should it be deemed an advantage.

5. Device for Insuring Leak-Proof Seals. A modified head assembly for the Fuel Pin Gas Sampling System has been designed and fabricated. This will permit use of the system to test 0.5 in. diam storage tubes for a gas tight seal of the soldered lid prior to removal from the inert atmosphere of the Disassembly Cell.

6. Saw for Opening Tungsten Capsules. An existing design was modified to provide a special remotely operated saw for opening tungsten capsules used in differential heat analysis investigations. This saw now accomplishes in ~ 40 min the severing of capsules which used to take ~ 6 h by the previous method.

III. MICROSTRUCTURAL ANALYSIS EQUIPMENT AND DEVELOPMENTS

(J. H. Bender, D. D. Jeffries, K. A. Johnson, J. L. Lehmann, H. D. Lewis, K. L. Walters)

A. New Blister Improvements

1. New Metallograph. The new Leitz remote metallograph has been installed and is performing very well. The optical quality of the micrographs on irradiated materials is excellent.

2. New Metallograph Stage. A new, precision, electrical, driver stage was installed on the remotized B and L metallograph.

3. Ion Gun Services. The base plate and vacuum equipment were installed in the new blister for use with the ion gun etching system when that development is completed.

4. Transfer Port. The new removal port has made it much easier to remove the autoradiographs (very low-level contamination) from the system.

5. Sample Hold-Down Weights. Hold-down weights for the samples were developed which aid considerably in improving sample orthogonality versus the X-Y stage motion.

B. Polishing and Grinding Hot Cell Improvements

1. Rotary Lap Units. Two Whirlamet rotary lap units (one for each cell) were remotized and are now being used as backup to the multiple system and for special handling such as touch-up or extra grinding.

2. High Pressure Impregnation. High pressure (~ 2000 psi Ar) impregnation systems (two) have been designed and fabricated for both unirradiated (glovebox) and irradiated samples. These systems have led to both qualitative and quantitative improvements, especially in the irradiated fuel samples. The pore and crack filling has, in samples examined to present, preserved better morphology and more delicate features than have been previously observed. No damage from the high pressure impregnation has been as yet detected. Quantitative improvements derive primarily from the holes and cracks being filled i.e. easier and improved cleaning and better controlled etching. While not confirmed yet, it should also ease and improve handling of sodium-containing fuel for similar reasons.

3. Improved Fixture for Sample Holder. New, improved, multiple-sample holder loading and unloading fixtures were designed, fabricated, and found to work well in-cell.

C. Ion Etching

A stable, controllable, ion gun and vacuum configuration were developed and a number of metallic materials were etched. Optimization of conditions, i.e. material type versus gas pressure, beam current, accelerating voltage, specimen to gun distance, and specimen angle to beam is being investigated. A version of the above design is being fabricated for eventual remote use on irradiated materials.

D. Programming

A program IMAGE has been written to handle the Quantimet data. This code will be discussed in detail in a topical report now being written.

E. Printer-Processor

The automatic printing and processing equipment is on hand, and engineering installation drawings are complete. Darkroom construction and installation of services has not been completed as yet.

F. Scanning Electron Microscope

The upgrade of the x-ray energy spectrometer on the scanning electron microscope was successful, allowing much higher count rates and improved resolution from 207 to 167 ev.

A transfer cask and shielded specimen holder for irradiated SEM samples were designed and fabricated, and specimen handling techniques were being developed.

G. Quantimet Instrument

Some pattern recognition capability has been added to the Quantimet 720 so that the instrument can now also size and sort on area, perimeter, and feret diameters, and it can also size and sort on feret diameters and intercepts in both horizontal and vertical directions. The 720 was of considerable assistance in processing the round-robin samples (see below Section VI). The 720 is now being applied to irradiated fuel.

IV. HOT CELL FACILITY AT DP WEST

(F. J. Fitzgibbon, M. E. Lazarus, J. M. Ledbetter, C. D. Montgomery, J. R. Phillips, J. W. Schulte, O. Serna, J. R. Trujillo, R. F. Velkinburg, J. B. Weber)

Relatively few items remain to be completed before the diagnostic equipment, as planned for the DP West hot cells, is ready to accept pins at the rate of approximately 150 per year. Therefore this section of the report is considered complete with the material contained in this "Fiscal Year 1972 Sixth Annual Report". Future work will be reported as contributions to the overall examination program.

The first hot operations were performed in this facility in late June when profilometry measurements were made on two irradiated fuel pins from HEDL.

A. Gamma Scanning Equipment, Mechanical

Installation of the gamma scanning equipment in building 401 is nearly complete. A modification has been made to the fuel element handling portion of the equipment to improve the alignment of the fuel element in front of the scanner. This alignment device is similar to the centering device used on the profilometer.

Other items completed during this fiscal year are:

1. Collimators completed except for certified inspection, which is in progress.
2. Safety devices added to prevent damage to the mechanical system in case of operator errors.
3. Safety devices added to the detector shield assembly to prevent the shield from falling in case of mechanical failure or earth tremors.

B. Electro-Optical Profilometer

The Electro-Optical profilometer has been installed at DP West and has been used to profile two HEDL fuel elements. The profilometer together with Data Acquistion system are operating satisfactorily at slow speed (12 in./min). Data Acquisition problems have not been solved at high speed (60 in./min), and a considerable amount of work may be necessary to obtain operation at this speed.

Other items completed during this fiscal year were:

1. Safety switches installed to prevent damage to the mechanical stage during the training of operators.
2. A computer program written to translate the data on magnetic tape on a plot on 35-mm film.
3. A computer program written to correct data for zero and span shifts.
4. A detailed operating procedure written for operating the profilometer equipment.
5. A high precision standard (tolerances to ± 30 μ in. designed and used to check profilometer linearity which was better than ± 100 μ in. over a .020 in. field of view. Note: This linearity check was done with standard remaining centered in the field of view to better than ± 0.001 in.
6. A set of standards designed and built to cover the normal range of fuel element pins and capsules. (The standards have an accuracy of better than ± 50 micro-inches).
7. The short-arc xenon lamp installed. (This lamp decreased some of the error caused by fuel element side motion but not as much as had been expected).
8. A fixture installed to center the diameter adjustment rollers to minimize the effect of bowing and general asymmetry, see Fig. 401-2.

The vendor of the optical sensing system, Physitech, has indicated that some improvements can now be made to their system which will "optically re-center the fuel elements in the field of view. Investigation of a different optical profilometer system is also under way.

Fig. 401-2. Fuel Element Centering Fixture for Optical Profilometer

C. Pulsed Eddy Current Scanner

A pulsed-eddy-current, fuel-pin scanning system will be installed at DP West 401. The mechanical system has been designed and built and is now at GMX-1 for checkout and installation of the electronic sensors. A four channel recorder has been obtained and was installed in Cell 2.

D. Macro-Photography

The macro-photography system has been installed. The camera stand has been modified to allow easy removel and replacement at the cell face to give the operator more room when photographs are not being taken.

E. Fission Gas Sampling System

The fission gas sampling system together with a system for obtaining a second fission gas sample has been installed at DP West. The system is leak-free and is presently undergoing final checkout.

V. ANALYTICAL CHEMISTRY

1. Gamma Scanning

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

The computer-controlled gamma scanner was installed in a modified office trailer adjacent to the examination hot cells at DP West. Installation of a gas (CF_3Br) fire control system in the trailer was completed, and the air conditioning unit is being installed.

Tungsten and lead collimators were fabricated and radiographed to ensure the absence of significant voids that would perturb their collimating ability. The collimators were precisely measured to provide input data for the COLLIM computer code which was developed to simulate the beam shaping response of any arbitrary collimating slit system consisting of up to ten collimators. The final alignment of the collimators was completed as the collimators were inserted into their positioning holders. An adapter for the scanning mechanism was designed to ensure that the fuel pin centerline was located at the center of the collimating slit. As the scanner response was dependent upon the source (fuel pin) position with respect to the collimating slit centerline, this adapter was needed to reduce to a minimum the effect of bow or twist in the fuel pins examined.

This facility in its new location is scheduled to be operational early in the first quarter of FY 1973.

In addition to the usual gross gamma and other scans of various fuel elements, as described elsewhere in this report, special scans of the natural UO_2 axial blanket of four fuel pins, NUMEC A-8, A-9, A-10, and A-11, were made because the gross gamma scans of these regions showed anomalous regions of high activity. Eash of these fuel pins contained a short UO_2 insulator pellet, a 14.2 in. $U_{0.8}Pu_{0.2}O_2$ fuel column, and a 6.25 in. natural UO_2 upper axial blanket column. Complete gamma-ray spectra were collected at 0.020 in. intervals, and the spectra were unfolded to determine the isotopic distributions of the fission products and activation products over the 6.25 in., UO_2, axial blankets. The two isotopes causing the anomalous increase in gross gamma activity were ^{137}Cs and ^{134}Cs. The isotopic distributions of these two isotopes for NUMEC A-10, see Figs. 401-3 and -4, respectively, show the significantly different distributions which indicate that migration mechanisms probably are different. The difference in distributions may be related to the half lives of the I and Xe precursors. The precursors of ^{137}Cs and ^{134}Cs are ^{137}I(24s) and ^{137}Xe(42m) which have relatively short half lives compared to the ^{134}Cs precursors, ^{133}I(21 h) and ^{133}Xe(5.27d). The ^{134}Cs distribution is the result of the migration to the gas plenum of the ^{133}I or ^{133}Xe which then beta decays to ^{133}Cs. The ^{133}Cs is neutron

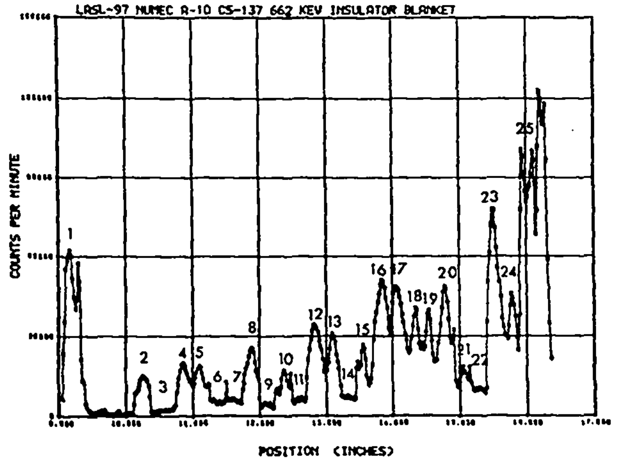

Fig. 401-3. ^{137}Cs distribution in UO_2 insulator blanket of NUMEC A-10.

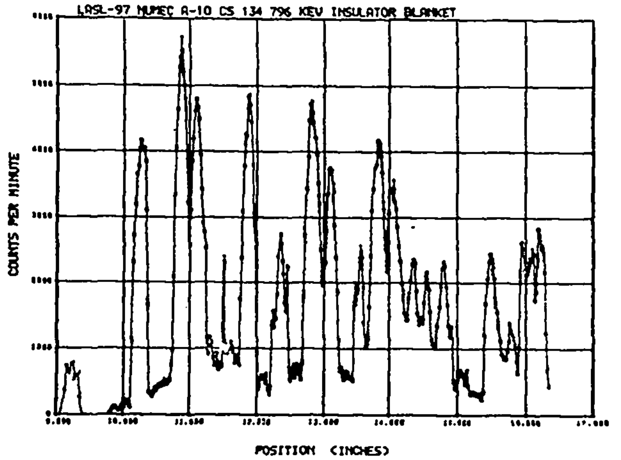

Fig. 401-4. ^{134}Cs distribution in UO_2 blanket of NUMEC A-10.

activated to ^{134}Cs.

The ^{137}Cs and ^{134}Cs isotopes collected preferentially on specific UO_2 pellets in the axial blanket column. To determine if the cesium activity could be related to the oxygen contents of the specific pellets, analyses were made for total oxygen in pellets having high cesium activity was directly related to the oxygen contents. Three additionel samples were obtained from the UO_2 region of NUMEC A-8 and also from A-10. Analyses for total oxygen, see Table 401-I, showed that the samples with oxygen contents above 11.8% have higher cesium concentrations on their surfaces than pellets with lower oxygen contents. The cesium isotopes may be preferentially forming stable oxides with the pellets having the higher contents of oxygen. We concluded that the ^{137}Cs and ^{134}Cs isotopic distributions are probably dependent uppn the half-lives of the precursors, and that the cesium located outside of the fuel column concentrates to a greater extent on UO_2 blanket pellets having higher total oxygen content.

TABLE 401-I

CESIUM ACTIVITIES AND OXYGEN CONTENTS IN FUEL PELLETS

Fuel Pin	Pellet Designation	Cesium Activity	Oxygen, wt.%
NUMEC A-8	1 & 2	low	11.72 ± 0.03
NUMEC A-8	4 & 7	high	11.89 ± 0.03
NUMEC A-8	5 & 6	low	11.73 ± 0.03
NUMEC A-10	16 & 17	high	11.87 ± 0.03
NUMEC A-10	21 & 22	low	11.64 ± 0.03
NUMEC A-10	23 & 25	high	11.81 ± 0.03

2. Determination of U and Pu in Irradiated Fuels (J. W. Dahlby)

Controlled potential coulometry was shown to be satisfactory for determining U and Pu without chemical separation of the U and Pu from each other or from the fission product elements in irradiated fuels having undergone up to 6 at.% burnup. The U was measured by integrating the current while reducing U(VI) to U(IV), and then subtracting a blank obtained by again reducing the same sample after a 6-min waiting period. The Pu was determined by electrically oxidizing the Pu(III) to Pu(IV), and then reducing the Pu(IV) to Pu(III). This oxidation-reduction cycle was repeated until successive integrated currents during the oxidation part of the cycle agreed within ± 2 mV or ± 2 μg of Pu. Small samples (approximately 1 mg of fuel) were analyzed for U and Pu with a precision of 0.5% relative standard deviation.

The analysis of fuels having burnups greater than 6% is adversely affected by the high radioactivity and fission product contents. Because of this, separations of the U and Pu from the highly radioactive fission products were investigated. Precipitation separations, being rapid and easy to perform under remote conditions, were tried first. The most promising separation involved precipitation of the U, Pu, and some fission products by adding NH_4OH. The U was selectively dissolved in basic $NH_2OH \cdot HCl$ solution. Greater than 95% of the β-γ active fission products were removed from the U by this separation, and the recovery of U was 99.6%.

The investigation of quantitative separations of U and Pu from fission products is continuing.

3. Analytical Chemistry Quality Assurance Program
(J. W. Dahlby)

An Analytical Chemistry Quality Assurance Plan and 22 quality assurance procedures were written for Project 401, and these documents were approved by the Quality Assurance Coordinator. The scope and critical steps of each operation were described to ensure that approved procedures were followed in all analyses and tests performed on materials in the postirradiation examinations of fast breeder reactor fuels. The standards, calibrations, and conditions used for each analysis or test were stressed in these procedures. Certification of analysts and distribution of these procedures to the certified analysts are in progress. An orientation lecture for everyone involved in this project is to be scheduled.

The quality assurance procedures written for Project 401 include:

1. Electron Microprobe Examination of Unirradiated Fuels
2. Gross Gamma Scan Analysis in Hot Cells
3. Multispectral Gamma Scanning in Hot Cells
4. Mass Spectrometric Analysis of Irradiated Fuel Pin Gas and Cover Gas
5. Two-Dimension Gamma Scanning in Hot Cells
6. Electron Microprobe Examination of Irradiated Fuel Pins and Other Highly Radioactive Materials
7. Calibration of Weights
8. Calibration of Volumetric Glassware
9. Calibration of a Capillary Trap and Monometer for Oxygen Determination
10. Determination of Crucible Temperature
11. Calibration of Thermocouples
12. Determination of Oxygen in Irradiated Fuels and Cladding Materials
13. Determination of Carbon and Hydrogen in Irradiated Fuel and Cladding
14. Dissolution of Irradiated Material
15. Determination of Atom Percent Fission in in Uranium and Plutonium Fuel
16. Determination of Manganese-54 in Irradiated Iron Flux Wire
17. The Coulometric Determination of Uranium and Plutonium in Irradiated Fuels
18. The Determination of Iron in Plutonium Fuels
19. Spectrochemical Analysis of Irradiated Fuel for Metallic Impurities
20. Spectrochemical Measurement of Metallic Impurities in Sodium
21. The Spectrochemical Measurement of Sodium in Fuel Solutions
22. Spectrographic Determination of Metallic Constituents in Stainless Steel

4. Determination of O_2 in Irradiated Reactor Fuels and Cladding
(C. S. MacDougall)

Two reliable methods for determining O_2 were modified for hot cell operations and applied to analyses of irradiated materials. In either method the sample is reacted at high temperature, approximately 2000°C, with C to convert the O_2 to CO and CO_2 which are measured. Although one reaction furnace suffices for analyses of various types of materials, two analytical finishes are required depending upon the O_2 content of the sample. The small amount of CO_2 obtained from traces of O_2 in carbide fuels or in claddings is measured micromanometrically. Larger quantities of CO_2 with some CO are generated from oxides, and these product gases are measured gravimetrically. Modifications necessary for remote operation involved adapting equipment for manipulator handling. In-cell tests show that the method is unbiased. The measured relative standard deviations are ± 0.4% in determining O_2 in irradiated oxide fuels and ± 10% for O_2 contents at trace levels.

The method and apparatus have been in routine use for the past year. Oxide fuels with burnups of 6.1 to

8.5% have been analyzed with no apparent difficulty. Cladding samples from pins having burnups as high as 10% have been successfully analyzed for O_2 after removal of all traces of fuel and Na coolant.

VI. REQUESTS FROM DRDT

A. Examination of Unirradiated Materials

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

1. Fuels. LASL has participated in an as-polished metallography round-robin with HEDL and several other laboratories. Careful mechanical density measurements were made on 20 samples, and 5 samples each were prepared in the hot-cell system and the glovebox system for optical microscopy. The resulting photomicrographs were intensively examined using the Quantimet and the IMAGE code. The results were sent to HEDL for reporting when all laboratories completed this phase of the round-robin.

Electron microprobe and x-ray examinations have been completed on 10 unirradiated samples from WARD.

2. Fuel Pins. Nineteen UNC pins (to be followed by LASL) were measured on the Optical Profilometer. The pins were numbered UNC-241 through UNC-259.

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)

Battelle Memorial Institute: Two capsules were received on April 25, 1972 and the following operations and the following operations and examinations were performed.

TABLE 401-II

POSTIRRADIATION EXAMINATIONS OF BMI MATERIAL

Examination	Capsule Identity
1. Visual Examination	BMI-1-4, -2-5
2. Contamination Swipes	BMI-1-4, -2-5
3. Radiation Measurements	BMI-1-4, -2-5
4. Radiography	BMI-1-4, -2-5
5. Photography (Full Length)	BMI-1-4, -2-5
6. Photography (Incremental)	BMI-1-4, -2-5
7. Temperature Measurement	BMI-1-4, -2-5
8. Gamma Scanning[a]	BMI-1-4, -2-5

[a] Gamma Scanning included four gross scans and two complete spectral scans on each capsule.

General Electric Company: On February 14, 1972, five irradiated fuel assemblies were received from GE VAL. Examinations performed on these assemblies are tabulated below.

TABLE 401-III

POSTIRRADIATION EXAMINATION OF CAPSULES FROM GE

Examination	Capsule Identity
1. Visual Inspection	F4E, F4A
2. Preliminary Measurement	F4E, F4A
3. Photograph (Full Length)	F4E, F4A
4. Radiography	F4E, F4A
5. Cover Gas Sampling	F4E, F4A
6. Clad Removal	F4E, F4A

TABLE 401-IV

POSTIRRADIATION EXAMINATION OF PINS FROM GE

Examination	Pin Identity
1. Visual Inspection	F4E, F4A, F12P, F12Q, F9C-13
2. Photography (Incremental w/wire wrap and w/o wire wrap)	F4E, F4A
3. Removal ow Wire Wrap	F4E, F4A
4. Photography (Full Length)	F4E, F4A, F12P, F12Q, F9-C-13
5. Profilometry	F4E, F4A, F12P, F12Q
6. Fission Gas Sampling	F4E, F4A, F12P, F12Q, F9C-13
7. Diameter Measurements (By micrometer on bent pin)	F9C-13

The gamma scanning shown below was completed on five fuel pins and/or capsules:

TABLE 401-V

GAMMA SCANNING OF GE MATERIALS

Fuel Pin Identity	Number of Gamma Scans	
	Gross	Complete Spectral
GE-F4E	4	1
GE-F4A	7	1
GE-F12Q	2	1
GE-F12P	2	1
GE-F9C-13	10	2

Spectral unfolding of ^{95}Zr and ^{95}Nb was used to determine the distributions of each isotope.

Mass spectrochemical analyses of the capsule gas in GE-F4E and GE-F4A were completed, in addition to analyses of the pin gases in GE-F9C-13, Ge-F12Q, GE-F12P, GE-F4A, and GE-F4E.

Microstructural examinations consisting of macrophotography, alpha and beta-gamma autoradiography, and optical microscopy (including mosaics) were carried out in Ar atmosphere on 2 fuel-clad specimens from GE-F9C-13.

Melting point determinations of irradiated mixed oxide fuel specimens are reported under the Project 463 "Fuel Properties" section of this report.

Gulf United Nuclear Fuels Corporation: Eleven capsules previously designated ad UNC were received on September 10, 1971 following irradiation in EBR-II. The examinations performed are listed in Table 401-VI.

Examinations performed on the pins and sections are shown in Table 401-VII.

In addition, the fission products on a suspected crack from the pin surface of UNC-194 were identified by analyzing contamination wiped from the surface with tissues (swipes).

TABLE 401-VI

POSTIRRADIATION EXAMINATION OF GU CAPSULES

	Examination	UNC Capsule Identity
1.	Visual Inspection	UNC-187, -189, -191, -192, -194, -195, -197, -198, -200, -206, -208
2.	Measurement of Contamination	Same as in Item 1
3.	Measurement of Temperature	Same as in Item 1
4.	Center Point Balance	Same as in Item 1
5.	Micrometer Measurement	Same as in Item 1
6.	Radiography	Same as in Item 1
7.	Photography (Full Length	Same as in Item 1
8.	Cover Gas Sampling	Same as in Item 1
9.	Na and Clad Removal[a]	Same as in Item 1

[a] Na melting and clad removal of UNC-194 and -200 were performed in an inert atmosphere. Cover gas analysis indicated that those two pins were breached.

TABLE 401-VII

POSTIRRADIATION EXAMINATION OF GU PINS

	Examination	UNC Pin Identity
1.	Micrometer Measurements	UNC-138, -146
2.	Center Point Balance	UNC-138, -146
3.	Photography (Incremental)	UNC-138, -146, -187, -189, -191, -192, -194, -195, -197, -198, -200, -206, -208
4.	Fission Gas Sampling[a]	UNC-107, -108, -109, -111, -112, -187, -189, -191, -192, -194, -195, -197, -198, -200, -206, -208
5.	Profilometry	UNC-187, -189, -191, -192, -195, -197, -198, -200, -206, -208
6.	Sectioning	UNC-92, -96, -99, -104, -107, -108, -109, -111, -112

[a] No gas was available for analysis because of the ruptured condition of the pin cladding of UNC-107 and -108.

Gamma scanning was applied to the nondestructive examination of the following fuel pins in Table 401-VIII.

The shielded electron microprobe was used for examining cross section samples of UNC-126, -219, -107H, -92H, and -96H.

Disintegration rates for ^{54}Mn were determined on iron flux wires in the following eleven pins: UNC-96, -99, -104, -107, -108, -109, -111, and -112.

The cover gas and pin gas were analyzed mass spectrometrically in the following eleven pins: UNC-187, -189, -191, -192, -194, -195, -197, -198, -200, -206, and -208. Also fission gases from the fuel pins UNC-109,

TABLE 401-VIII

GAMMA SCAN OF GU FUEL PINS

Fuel Pin Number	Number of Gamma Scans	
	Gross	Complete Spectral
UNC-138	4	--
UNC-146	4	--
UNC-187	4	--
UNC-192	4	1
UNC-194	4	2
UNC-195	4	2
UNC-197	8	2
UNC-198	4	2
UNC-200	4	1
UNC-206	7	1
UNC-208	4	1

TABLE 401-IX

MICROSTRUCTURAL ANALYSIS OF GU PINS

UNC Pin Number	Type	
	Fuel + Clad	Clad or Structurals
92	5	
96	5	
99	4	1
104	4	1
107	3	1
108	1	1
109	3	1
111	2	1
112	1	1
126	1	
219	1	

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

Microstructural examinations consisting of macrophotography, alpha and beta-gamma autoradiography, and optical microscopy (including mosaics) were carried out in an Ar atmosphere on specimens as shown in Table 401-IX.

Two samples were also prepared for electron microprobe including pre- and post-EMX photomicroscopy.

Hanford Engineering Development Laboratory: Two pins from the PNL-17 series were received on December 2, 1971, and eleven pins from the HEDL-P-17A series were received on February 22, 1972. Examinations made on these pins are tabulated in Table 401-X.

Density measurements were made on 4 cladding specimens from each of PNL-17-7 and PNL-17-33 pins.

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

Pin P-17A-27 was damaged in handling during the initial examination period. The damage consisted of a 45° bend in the plenum area 6.5 in. below the top of the pin and a 3-in.-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 a measurable diameter increase on this low-burnup experiment.) Documentary photographs were taken of the bent pin and

TABLE 401-X

POSTIRRADIATION EXAMINATION OF HEDL MATERIAL

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

*This was the first use of the Optical Profilometer on irradiated fuel pins.

forwarded to the Experimenter. The radiography and gamma scanning examinations were carried out after the 6-1/2 in. gas plenum section was removed in the inert disassembly box.

Gamma scanning, both gross and complete spectral scans, was applied to the nondestructive examination of HEDL fuel pins as tabulated below.

TABLE 401-XI

GAMMA SCANNING OF HEDL PINS

	Number of Gamma Scans	
Fuel Pin Number	Gross	Complete Spectral
PNL-17-7	4	1
PNL-17-33	4	3
HEDL-P-17A-5	4	-
HEDL-P-17A-16	4	-
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	-
HEDL-P-17A-33	4	1
HEDL-P-17A-27	4	2

Mass spectrometric analysis was applied to the pin gas samples from PNL-17-7, -17-33, HEDL-P-17A-5, -16, -17, -18, -19, -20, -26, -27, -29, -31, and -33.

Cross section samples of PNL-17-7 and -17-33 were analyzed for burnup.

Microstructural examinations consisting of macrophotography, alpha and beta-gamma autoradiography, and optical microscopy (including mosaics) were carried out in an Ar atmosphere on specimens as listed in Table 401-XII.

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

Capsule K-37B was received on April 25, 1972 and the examinations and operations performed on this capsule are described in Table 401-XIII.

TABLE 401-XII

MICROSTRUCTURAL ANALYSES OF HEDL MATERIALS

HEDL	Type	
Pin No.	Fuel + Clad	Clad or Structurals
PNL-17-7	2	4
PNL-17-33	2	4
PNL-17A-18	5	
PNL-17A-26	3	

TABLE 401-XIII

POSTIRRADIATION EXAMINATION OF CAPSULE FROM LASL

Examination	LASL Capsule Identity
1. Visual Inspection	K-37B
2. Contamination Swipes	K-37B
3. Radiation Measurement	K-37B
4. Photography (Full Length)	K-37B
5. Photography (Incremental)	K-37B
6. Radiography	K-37B
7. Temperature Measurement	K-37B
8. Gamma Scanning[a]	K-37B

[a] Gamma Scanning included four gross scans and one complete spectral scan.

Nuclear Materials and Equipment Corporation: Examinations made on material from NUMEC are being followed by representatives from ANL. The examinations performed on these materials during FY 1972 are tabulated below.

Nondestructive gamma scanning was used in examining the following NUMEC fuel pins.

TABLE 401-XIV

GAMMA SCANNING OF NUMEC PINS

	Number of Gamma Scans	
Fuel Pin Number	Gross	Complete Spectral
NUMEC A-1	4	1
NUMEC-A-8	2	3
NUMEC A-10	2	3

Cross section samples from NUMEC-A-10A, -A-10H, -A-11F, -B-11 were examined using a shielded electron microprobe.

A cross section sample (NUMEC-A-5) of fuel and cladding was dissolved and analyzed for burnup.

The fission gases in the fuel pins NUMEC-A-1 and NUMEC-A-6 were analyzed mass spectrometrically.

Microstructural examinations consisting of macrophotography, alpha and beta-gamma autoradiography, and optical microscopy (including mosaics) were carried out in an Ar atmosphere on 7 fuel-clad specimens from A-10, on 5 fuel-clad specimens from A-11 and on 4 fuel-clad specimens from B-11. In addition, two samples were prepared for the microprobe including pre- and post-EMX photomicroscopy.

A 2 in. section of NUMEC pin A-1 containing the UO_2-(U Pu)O_2 interface was shipped to ANL on November 3, 1971. On November 10, 1971, twelve sections of fuel-cladding and three sections of cladding were shipped to ORNL. These sections were removed from NUMEC pins B-1, A-5, A-6, A-8, A-9, A-10 and A-11.

Oak Ridge National Laboratory: Capsule ORNL-43-N2 was received on April 25, 1972 and the following examinations have been performed.

TABLE 401-XV

POSTIRRADIATION EXAMINATION OF ORNL MATERIAL

Examination	Capsule Identity
1. Visual Examination	ORNL-43-N2
2. Contamination Swipes	ORNL-43-N2
3. Radiation Measurements	ORNL-43-N2
4. Radiography	ORNL-43-N2
5. Photography (Full Length)	ORNL-43-N2
6. Photography (Incremental)	ORNL-43-N2
7. Temperature Measurement	ORNL-43-N2
8. Cover Gas Sampling	ORNL-43-N2
9. Clad Removal	ORNL-43-N2
10. Diameter Measurement	ORNL-43-N2
11. Segment Separation	ORNL-43-N2
12. Profilometry (segments 1,2,3)	ORNL-43-N2
13. Fission Gas Sampling	ORNL-43-N2

The nondestructive tests on ORNL-43-N2 consisted of 5 gross gamma scans and 2 complete spectral scans.

The capsule gas in ORNL-43-N2 was analyzed mass spectrometrically.

Other Material From Experimenters: Discussions have been held with GE, ANL, and ORNL personnel relative to shipping additional pins to LASL for examination in FY 1973. Meetings are scheduled with HEDL personnel during August and September to coordinate the examination of HEDL pins at LASL.

VII. QUALITY ASSURANCE PROGRAM

The Quality Assurance Program was instituted as requested by DRDT, and a full-time employee is assigned to the 401 and 463 programs. Hot Cell Procedures were revised to conform to the Quality Assurance Requirements. Training and certification of operating personnel was started during Fiscal Year 1972, and lectures describing the importance of the Quality Assurance Program at LASL have been scheduled for July 1972.

Methods for handling, documentation, and storage of standards used in the diagnostic examinations have been made more rigorous as required in the Quality Assurance Plan.

VIII. PUBLICATIONS

1. J. R. Phillips, G. R. Waterbury, G. H. Mottaz, and J. N. Quintana, "New System for Gamma Scanning Fuel Elements," to be presented at and published in the Proceedings of the 20th Conference on Remote Systems Technology, Idaho Falls, American Nuclear Society, September 19-21, 1972.
2. C. S. MacDougall, M. E. Smith, and G. R. Waterbury, "Remotized Apparatus for Determining Oxygen in Irradiated Reactor Fuels and Cladding Materials," to be presented at and published in the Proceedings of the 20th Conference on Remote Systems Technology, Idaho Falls, Idaho, American Nuclear Society, September 19-21, 1972.
3. C. S. MacDougall, M. E. Smith, and G. R. Waterbury, "The Determination of Oxygen in Irradiated Reactor Fuel and Cladding Materials," LA-4971, Los Alamos Scientific Laboratory (1972).
4. J. W. Dahlby, G. R. Waterbury, C. D. Montgomery, and T. Romanik, "Application of the Sealed-Tube Method to Remote Dissolution of Irradiated Refractory Materials," Proceedings of 19th Conference on Remote Systems Technology, American Nuclear Society, October 1971.

5. J. W. Dahlby, R. M. Abernathey, M. E. Smith, J. E. Rein, and A. Zerwekh, "Analysis of Irradiated Fuels and Measurements of Interstitials," to be presented at the 16th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., October 24-26, 1972.

6. J. R. Phillips, J. W. Schulte, and G. R. Waterbury, "The Use of High-Resolution Gamma-Ray Spectrometry for Detecting Failure of Cladding in Encapsulated Fast Reactor Fuel Pins," Proceedings of the 19th Conference on Remote Systems Technology, American Nuclear Society, October 1971.

7. J. R. Phillips, E. A. Hakkila, G. M. Matlack, and J. Bubernak, "Special Instrumental Methods of Analysis," to be presented at the 16th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., October 1972.

8. C. D. Montgomery, M. G. Chavez, and M. E. Lazarus, "Development of Ancillary Equipment for Use in Hot Cell Facilities," to be published in Proceedings of the 20th Conference on Remote Systems Technology, American Nuclear Society, September 1972.

9. D. D. Jeffries, J. H. Bender, and K. A. Johnson, "Improvements in Remote Metallography in Inert Atmospheres," to be presented at the 20th Conference on Remote Systems Technology, American Nuclear Society, September 1972.

10. K. A. Johnson, "Scanning Electron Microscopy of LMFBR Materials," to be published in the 1971 IMS Proceedings, Fourth Annual Technical Meeting, International Microstructural Analysis Society.

11. J. H. Bender, "Sample Preparation and Equipment Problems Associated with Re-Cycled Purified Atmospheres," to be published in the 1971 IMS Proceedings, Fourth Annual Technical Meeting.

12. K. A. Johnson, "Image Analysis Statistics -- Part II," to be published in the 1971 IMS Proceedings, Fourth Annual Technical Meeting.

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,
R. Walker, C. W. Bjorklund, and J. G. Reavis

1. Carbide Production

The preparation of pure, single phase $(U_{.80}Pu_{.20})C_{.98}$ fuel for EBR-II irradiations was continued using previously described procedures and equipment.[1] A concerted effort was made to upgrade the existing process equipment so that operating conditions could be more precisely reproduced. Fuel for seven pins totaling 490 pellets was produced after the alterations, all of which exceeded fuel specifications.

During the course of routine production, radiographic examination indicated one batch of fuel contained several pellets which were end-capped. Subsequent batches contained an increasing number of end-capped pellets, and eventually laminated pellets were observed. Each phase of the production process was carefully analyzed and it was determined that the end capping phenomenon was due to a gradual deterioration of the pressing die and punches. New dies were ordered and have been received. It was also found that old dies could be lapped to remove scoring and when used with new punches could be put back into service.

2. Equipment Development

A high-temperature sintering furnace was installed and is now being used for all sintering operations. The high vacuum furnace is heated by tungsten mesh elements which can be operated in high vacuum, He, Ar, or N_2. This unit is located in a recirculating inert atmosphere glovebox which operates typically at > 10 ppm H_2O and > 5 ppm O_2. Furnace and glovebox windows were calibrated prior to installation. A black body hole in the sintering crucibles is used to provide for accurate temperature measurements. Since carbides are normally sintered in an Ar atmosphere, a Ti gettering furnace was incorporated into the system rather than a standard U chip furnace. With a Ti charge, the effluent gas purity was equal to that obtained using U and the charge life was extended at least 10-fold.

A new hydrogen treatment facility was designed, fabricated and installed in an existing recirculating inert atmosphere glovebox. High vacuum and UHV design principles were incorporated into the design and construction of the system to minimize any potential contamination. Hydrogen containing only a few parts per billion impurities is obtained from a Pd alloy diffusion cell. The reaction chamber has a capacity approximately 6 times larger than the existing furnace. This unit will be placed in service in the near future.

In addition to equipment associated with carbide production, facilities were installed for the preparation of nitride fuel pellets. One recirculating inert atmosphere glovebox contains equipment for low temperature hydriding and nitriding of U and/or Pu, a centrifugal mill for comminution, a balance and a press. This glovebox facility is complete and ready for use. In another recirculating inert atmosphere glovebox a high temperature, tungsten mesh sintering furnace is being installed for use in nitride sintering and the synthesis of UN.

3. Process Development

a. Densification

Pellets of > 93% theoretical density were produced from carbides which were spex ground only and from material which was spex ground and then ball milled. The addition of ball milling in the comminution procedure typically reduced the mass median diameter of the powder from 6.5 to 2.4μm and tended to produce slightly higher density pellets. Although reduced particle size decreased the intragranular void space, the increase in intergranular void space negated much of the effect. Furthermore, an increase in the Fe or W content of the pellets was observed in powders which were treated in stainless steel or WC lined ball mills. Additional experiments are planned to determine optimum particle size.

Variation of the pressing parameters showed a significant effect on the pellet density only at very low pressing pressures, e.g., $\leq$ 10 tsi. Under these conditions low density pellets were produced. At higher pressing pressures the sintered pellet density was relatively constant at ~ 93% theoretical density. As the pressure was increased, the diametral shrinkage decreased so that, within limits, the finished pellet diameter could be controlled during the pressing operation.

The most significant variable affecting pellet density was sintering temperature. It was found that carbides could be sintered in Ar up to 1900°C in the new W-mesh sintering furnace without the formation of second phases. Most of the densification occurred during the first 4 hr of sintering. Prolonged or additional sintering increased the density only slightly.

b. Gas Chromatrography

Equipment and techniques have been developed and refined for gas chromatrographic analysis of the effluent gas stream from the hydrogen reduction furnaces used to adjust the carbon content of carbide fuel materials. The evolution of CH_4 from hyperstoichiometric (U, Pu) C during the H_2 treatment step in routine production runs was greatest immediately after H_2 was admitted to the furnace and decreased exponentially with time. After 36 hr., CH_4 evolution was barely detectable (a few ppm) and remained at this level for the duration of the run. However, chemical and metallographic analysis of one batch showed that reduction to single phase monocarbide was still incomplete at the end of the 36 hr. period, indicating that the reaction might be controlled by a relatively slow rate of escape of CH_4 from the solid as suggested by Harder, Read, and Sowden[2] and by Sowden, et al.[3] Additional supporting evidence was obtained when the hydrogen treatment of another standard batch of hyperstoichiometric carbide was monitored. Although CH_4 evolution had been only barely detectable during the last 30 hr of the 68-hr run, it increased by a factor of four during a 45-min period after power to the furnace was turned off with H_2 still flowing over the charge. During this interval, the furnace temperature dropped from 800° to 500°C, apparently causing the rate of escape of CH_4 to increase. The material from this batch was single phase after reduction.

Chromatographic equipment and techniques have also been shown to be very useful for monitoring the nitrogen contamination levels in the high purity Ar inert atmospheres in gloveboxes used for carbide production.

c. Carbide Production by Carbothermic Reduction of UO_2-PuO_2

The method preferred in the past at LASL for the small scale production of high purity, single-phase, uranium-plutonium monocarbide has been the direct reaction of the elements in an arc melter, even though this process is comparatively expensive. For large scale fuel fabrication operations, however, economics become more important. Pure oxides of U and Pu are more cheaply prepared than pure metals, making oxides the preferred starting material.

The preparation of (U, Pu) C by reduction of the oxides with graphite is not a new process, but most material synthesized using this reaction has contained a high level of oxygen or other impurities. An experimental program is being pursued at LASL to demonstrate that pure (low oxygen), single-phase $U_{0.8}Pu_{0.2}C$ can be prepared using improved carbothermic techniques.

As indicated above, the carbothermic reduction preparation of uranium-plutonium carbides is not a new procedure. There are, however, several unique features in the LASL process. The initial oxide-carbon mixture is intentionally made carbon rich to ensure the presence of sesquicarbide in the reaction product. This is done to maintain a large carbon activity to maximize the equilibrium CO pressure during the final stages of the reduction. This, in addition to a final high temperature treatment in high vacuum, is critical to the preparation of material having low residual oxygen contents. The steps used in this process are:

1. Ball mill and blend UO_2, PuO_2 and excess graphite,
2. Form low density powder compacts,
3. Heat in a high vacuum system at 1400 - 1700°C until CO evolution ceases,
4. Crush and comminute,
5. Heat in flowing H_2 at 800°C to remove higher carbides,
6. Press into pellets,
7. Sinter under Ar.

Only the first three steps of the process are regarded as developmental. Steps 4 through 7 are routinely used in preparation of MC pellets from arc melted ingots. The effort up to this time has not been to optimize the process, but rather to demonstrate feasibility. Times and batch sizes have been selected to fit into existing schedules and equipment.

In step 1, 75g batches of combined UO_2, PuO_2 and C powders were ball milled 20 hr. This mixture was then pressed into 0.5 in. dia by 0.5 in. high slugs and the reduction was carried out in vacuum in loosely covered graphite crucibles. Typical temperatures and

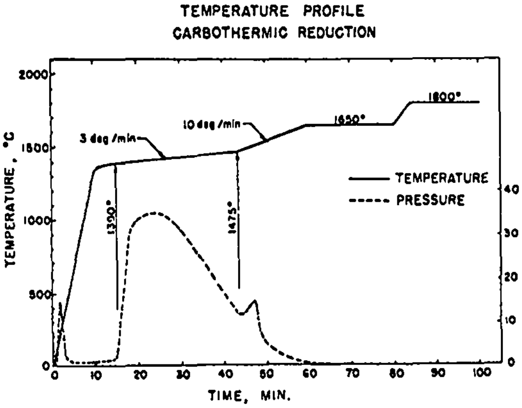

Fig. 463-1. Temperature and pressure as functions of time during a carbothermic reduction.

pressures are plotted as a function of time in Figure 463-1. Products of the reduction were sampled for analysis, then taken through process steps 4 through 7 and sampled again.

In an early series of experiments, the reduction was carried out in a small induction-heated furnace in which the maximum size of charge was about 15g. Using this apparatus, the brief exposure of the reduction product to air during transfer to the sampling area was the probable cause for the high oxygen concentrations found in these samples. Analyses of these products after process step 3 are shown in Table 463-I. As would be expected from the C analyses listed, these carbides contained M_2C_3 (shown by metallographic examination). These preliminary data were sufficient to demonstrate that low residual oxygen contents could be obtained using the process.

A later series of experiments based on a reduction batch size of 50g was run in a larger resistance-heated furnace which is capable of higher pumping speeds and thus lower pressures of CO in the reaction zone during reduction. The reduction products were analyzed for oxygen, but were not examined metallographically because of their extreme porosity. They were generally carried through steps 4, 6, and 7 and examined for M_2C_3 metallographically. The nominal carbon contents of the original MO_2 plus C mixtures and partial analyses of the products are listed in Table 463-II.

TABLE 463-I

CHEMICAL ANALYSIS OF CARBOTHERMICALLY PREPARED CARBIDES

Element	Gram-Atom/Mole of Carbide			Concentration, wt%		
	CBT-A	CBT-B	CBT-C	CBT-A	CBT-B	CBT-C
U	0.810	0.814	—	75.8	76.5	—
Pu	0.190	0.186	—	18.12	17.92	—
C	1.104	1.207	—	5.86	5.82	—
O	0.003	0.012	0.008	0.021	0.077	0.052

It can be seen from the results listed in Table 463-II that carbides containing very little oxygen can be produced. To do so, however, excess C must be present in the reaction mixture and sufficiently long reaction times must be used. The high oxygen concentration in the product of CR-7 was caused by insufficient reaction time above 1650°C. The reactants were held above 1650°C for only 6 min in CR-7, and for 90 min in CR-8. The high oxygen content of the product of CR-7 was reduced during sintering (CR-7S) by heating slowly (~5 deg/min) in vacuum between 1400° and 1625°. The furnace was then filled with Ar and heated to 1800° to sinter the pellets to produce densification.

The effect of carbon concentration on the oxygen level of the product can be seen by comparison of the products of experiments CR-8 and CR-9. The reaction conditions were very similar in the two experiments, but the

TABLE 463-II

SECOND SERIES OF DEVELOPMENTAL CARBOTHERMIC REDUCTIONS FOR THE SYNTHESIS OF $U_{0.8}Pu_{0.2}C$

Expt No.[a]	Original C Conc., wt.%	O Conc. in Product, ppm	M_2C_3 in Product, vol.%
CR-4	13.24	40	---
CR-4S	13.24	140	~60
CR-5	12.48	10	---
CR-55	12.48	40	~30
CR-6	12.29	110	---
CR-6S	12.29	50	~25
CR-7	12.12	0.22%	---
CR-7S	12.12	540	~15
CR-8	12.12	30	---
CR-8HS	12.12	125	~ 3
CR-9	11.92	475	---
CR-9S	11.92	520	< 1

---

[a] The suffix "S" refers to carbides taken through process steps 4, 6 and 7; HS refers to a carbide taken through process steps 4, 5, 6 and 7.

oxygen concentrations in the products are seen to be very different. The C concentration of 11.92 weight per cent in the reacting mixture of CR-9 may be at or slightly below the concentration needed to produce a carbide containing an acceptably low concentration of oxygen.

The estimates of M_2C_3 concentrations in the sintered products described in Table 463-II are qualitative and are based on examination of the microstructures of polished and stained specimens. The concentrations are qualitatively those that would be expected, based on the amount of C in the reacting mixtures. Comparison of the amounts of M_2C_3 in the products of CR-7S and CR-8HS illustrates the effectiveness of the conversion of M_2C_3 to MC by approximately 5 hr of H_2 treatment at 800°C. A standard production hydrogen reduction schedule would have eliminated the last traces of higher carbides.

d. Carbide Oxidation

In the production of $U_{.8}Pu_{.2}C$ the oxygen content of the material gradually increases from a few ppm in the feed to 200-300 ppm in the product. To produce material of this quality, extensive use is made of inert atmosphere gloveboxes. Although the problem of oxidation is not eliminated by the use of inert atmosphere gloveboxes, it is significantly reduced.

An indication of the extent and rate of oxygen contamination from the atmosphere of an inert glovebox was obtained from the following experiment. A sample of approximately 23 g of -250 mesh $U_{.80}Pu_{.20}C_{.98}$ powder was placed in a shallow, open 6 cm dia weighing dish and set aside in a glovebox. The weight gain was periodically measured over a period of several weeks. The results of these measurements are shown in Table 463-III. The magnitude of this weight gain is sufficient to change the carbide powder from single phase to multiphase material. On one occasion the glovebox atmosphere rapidly deteriorated due to a hole in a glove. During this 24 hr. period the weight gain was nearly 1000 ppm or 25 times normal. The weight gain was attributed to an increase in oxygen content and was confirmed by chemical analysis.

TABLE 463-III

OXIDATION OF CARBIDE FUEL IN AN INERT ATMOSPHERE GLOVEBOX

Glovebox No.	2	3
O_2 in atmosphere (ppm)	5	2
H_2O in atmosphere (ppm)	0.5	3
Days monitored	55	49
Wt increase/day (ppm)	40	47

In another experiment an entire batch of carbide was placed in a vacuum chamber at 1 x 10^{-5} torr or better. Portions of the powder were removed for pressing and sintering over a period of 3 weeks. No compositional change was observed between the first and last pellets produced thus demonstrating the applicability of vacuum as a storage medium for this process.

4. 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. They were received, unpackaged, inspected, and sampled for the following:

1. chemical analysis
2. spectrochemical analysis
3. determination of density
4. metallographic examination
5. x-ray powder diffraction analysis.

Approximately 14 pellets were received, but the exact number is undefined because most of the pellets were fractured. The largest chunks were identified by numbering, and kept separate during the sampling procedure.

The results of chemical analysis for major constituents of 4 pellets are shown in Table 463-IV.

The stoichiometry of the nitride is somewhat lower than expected, typical being $MN_{0.95}$ for the solid solution nitride.

The results of chemical analyses for minor contaminants are shown in Table 463-V. The O and Th concentrations are nominal, but the C content is somewhat

TABLE 463-IV

CHEMICAL ANALYSIS OF NITRIDE PELLETS

Sample No.	(concentrations in wt%) U	Pu	N	Calculated Formula
6	76.5	18.23	5.36	$(U_{0.816}Pu_{0.184}) N_{0.93}$
11	76.6	18.29	4.87	$(U_{0.816}Pu_{0.180}) N_{0.874}$
12	76.1	18.43	5.30	$(U_{0.808}Pu_{0.192}) N_{0.96}$
13	76.1	18.41	4.68	$(U_{0.808}Pu_{0.192}) N_{0.834}$
Misc. Chunks	--	--	5.26	--

TABLE 463-V

CHEMICAL ANALYSIS OF NITRIDE PELLETS[a, b]

(concentrations in ppm)

O	545	Cr	10
C	505	Mn	5
Th	10	Fe	20
Li	< 1	Ni	< 10
Be	< 1	Cu	< 2
B	< 1	Zn	< 20
Na	8	Sr	5
Mg	< 5	Cd	< 20
Al	< 10	Sn	< 5
Si	< 20	Pb	< 5
Ca	< 5	Bi	< 2

---

[a] Results for O, C, and Th are the average for four samples for chemical analysis.

[b] Results for all others are the average for three samples for spectrochemical analysis.

higher than normal for the industry. Results of spectrochemical analysis indicate that the cationic impurity levels are quite low.

The densities of several pellets were determined by immersion techniques. The results shown in Table 463-VI indicate densities that are generally between 93 and 94% of theoretical. The anomalous density of sample 2 is probably due to a large, closed, internal void and does not reflect the microscopic density of the material. Lattice dimensions of several samples were determined using Debye-Scherrer powder techniques and were found to be 4.8930 ± 0.0005 A.

TABLE 463-VI

NITRIDE PELLET DENSITIES

Sample	Density (g/cm^3)	% T. D.[a]
1	13.36	93.2
2	12.70	88.6
7	13.45	93.9
9	13.51	94.3
10	13.48	94.0

---

[a] Theoretical density = 14.33 g/cm^3

The metallographic examination of 5 samples is complete. Generally, the microstructures were found to be single phase with ≤ 0.5 vol % of a white appearing second phase in evidence. The "white phase" may be slightly more concentrated toward the pellet exteriors. The grain size is approximately twice as large near the pellet centers as near the edge. The pellet edges are composed of very small sized grains as compared to the centers. The pores or voids are of two general types:

a. large irregularly shaped pores located at or near grain triple points

b. by comparison, very small sized pores located in the grain interior.

One pellet was heated in Ar to approximately 1600°C, and then examined for possible microstructural changes. No changes were found.

B. EBR-II Irradiation Testing

(J. O. Barner, T. W. Latimer, 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. All of these programs have been consolidated at LASL. The status of ongoing experiments originated by all of these programs is included in this report.

Four series of LASL-orientated experiments are planned. The status of the first three series is described in Table 463-VII. All of 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 of these experiments is shown in Table 463-VIII. The test variables include fuel type, cladding cold-work, smear density, heating rate, operating temperature, fuel restraint, 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 at LASL from material synthesized using the arc-melting process. Material prepared by the carbothermic reduction process may also be used. The nitride fuel for the initial loadings will be supplied by Battelle Memorial Institute and will be prepared using the hydride-nitride process. As of mid-June, 1972, BMI had produced 12 batches of fuel and anticipated fabricating two additional batches. The material had not been received as of the end of FY 72. The cladding tubing will be Type 316 stainless steel 0.310 in. O.D. with a wall thickness of 0.012 in. The cladding was purchased through HEDL from Superior Tube Co. Both solution annealed and 20% cold worked tubing were purchased. The tubing complies, as nearly as possible, to the fuel element cladding specification RDT-E13-8. End plug material has been received from HEDL. The 20% cold worked, Type 316 stainless steel for the end plugs is a portion of the batch of bar

TABLE 463-VII

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, at.%	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	NDT
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[e]
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	X119B - in
K-46	3	$(U_{0.8}Pu_{0.2})C$	95	0.020	1150	30	2.3	X119B - in
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	X119B - in
K-50	2	$(U_{0.8}Pu_{0.2})C$	95	0.020	1400	45 - 50	3.1	X119B - in
K-51	2	$(U_{0.8}Pu_{0.2})C$	95	0.020	1400	45 - 50	3.1	X119B - in

---

[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% ^{233}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] *Reported in LA-4669 MS.*

TABLE 463-VIII

DESCRIPTION OF SERIES 4 EXPERIMENTS[a]

Experiment No.	Fuel Type[b]	Smear Density, %	Cladding[c]	Shroud	Peak Cladding Temperature, °F (°C)	Approximate Peak Centerline Temp., °F (°C)	Goal Burnup, MWD/MTM
52	C	82	SA	Yes	1060 (570)	1900 (1040)	65,000
53	C	82	SA	Yes	1170 (630)	2000 (1100)	100,000
54	C	82	SA	No	1170 (630)	2000 (1100)	100,000
55	C	82	SA	No	1060 (570)	1900 (1040)	65,000
56	C	82	SA	Yes	1160 (625)	2000 (1100)	100,000
57	C	82	CW	Yes	1050 (565)	1900 (1040)	100,000
58	C	82	CW	Yes	1160 (625)	2000 (1100)	100,000
59	C	82	CW	No	1050 (565)	1900 (1040)	100,000
60	C	85	SA	No	1050 (565)	1900 (1040)	65,000
61	C	85	CW	No	1060 (570)	1900 (1040)	100,000
62	N	82	SA	No	1050 (565)	2400 (1315)	65,000
63	N	82	CW	No	1170 (630)	2500 (1375)	100,000
64	N	82	SA	Yes	1170 (630)	2500 (1375)	100,000
65	N	82	CW	Yes	1180 (640)	2500 (1375)	65,000
66	N	82	CW	Yes	1070 (575)	2400 (1315)	100,000
67	N	82	SA	Yes	1080 (580)	2400 (1315)	100,000
68	N	82	SA	Yes	1050 (565)	2400 (1315)	100,000
69	N	85	SA	No	1070 (570)	2400 (1315)	100,000
70	N	85	CW	No	1060 (565)	2400 (1315)	65,000

[a] Heating rates will be in the range 38 to 40 kw/ft. All elements sodium bonded.

[b] C = 95% dense $(U_{0.8}Pu_{0.2})C$, 93% enriched ^{235}U.
N = 95% dense $(U_{0.8}Pu_{0.2})N$, 93% enriched ^{235}U.

[c] SA = solution annealed Type 316 stainless steel.
CW = 20% cold worked Type 316 stainless steel.
Both types are 0.310 in. O.D. by 0.286 in. I.D.

stock fabricated for the FFTF control rod structural components and complies to RDT-M-7-23T. Hold-down springs will be made from 0.031 in. dia., Type 302 stainless steel, FFTF driver fuel element spacer wire material. Shroud tubes with perforated slots are planned for use as a fuel restraint mechanism in 10 of the fuel elements; the shrouds will be made from Type 316 stainless steel that has a wall thickness of approximately 0.003 in. Approval in principle has been received from AEC and the final design of the shroud tubes and the fuel elements is currently underway.

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, is summarized in Table 463-IX, X, XI, and XII. A total of 63 capsules or elements originated by GUNFC are either in EBR-II or available for insertion. Subassembly X-142 is scheduled for removal from EBR-II at the goal burnup of 100,000 MWD/MTM for the lead capsules after EBR-II run 56 which is estimated to end in mid-August 1972. Capsule U261 has a 0.020 in. bow, but has been accepted for irradiation based on the maximum bow. However, the eddy current traces indicate a possible sodium bond defect between the element and the capsule. The apparent defect occurs at the point of maximum bow and is believed to be associated with the bow. An attempt to resolve the actual cause of the apparent defect is being made in conjunction with the EBR-II project.

Fuel element U255 from task 5100 has a tungsten inclusion in the lower weld. It is not felt that the weld can be repaired at this time. The element has been rejected for irradiation by the EBR-II project and will be replaced with a Type 316 stainless steel dummy element.

The nineteen singly clad task 5100 elements were nondestructively examined at LASL prior to shipment to EBR-II. Diameter measurements were made using the same profilometer that will be used after irradiation.

TABLE 463-IX

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	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-X

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	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	12.8	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.

In general, these confirmed the GUNFC micrometer measurements, but there was a tendency for the diameters measured using the profilometer to be a few ten-thousandths of an inch larger than those reported by GUNFC. The nondestructive fissile assay indicates that the ^{239}Pu content of the elements was 3% ± 2% higher than reported by GUNFC. The $^{235}U/^{239}Pu$ ratio was measured with less precision and indicates that the ratio is ± 5% of the value reported by GUNFC. Agreement between the two sites is gratifying.

The status of the nitride experiments originated by BMI is shown in Tables 463-XIII, XIV, and XV. A total of 14 encapsulated elements are in EBR-II. Twenty singly clad elements are at LASL for a series of nondestructive examinations. These examinations include radiography, profilometry, and fissile assay. Four of the elements, C-5-1, -2, -3, and -17, are believed to have air in the plenum and have been rejected for irradiation in EBR-II. The nondestructive examinations are expected to be completed by mid-August 1972.

The status of the nitride experiments sponsored by ORNL, Series O-N1, is shown in Table 463-XVI. These singly clad experiments are to be irradiated with the C-5 series. The seven O-N1 experiments are currently being nondestructively examined. Radiographic results indicate that three of the seven experiments may be rejected due to large fuel chips in the fuel-cladding annulus.

Two thermal irradiation experiments from ORNL will be examined. Both experiments are sodium-bonded nitride experiments from the ETR.

C. TREAT Irradiation Testing

(J. F. Kerrisk, D. G. Clifton, R. E. Alcouffe, K. L. Walters)

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 carried out on

TABLE 463-XI

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	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	1148	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
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	46,000	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]	0.016	0.015	He	2590	34.1	———	At EBR-II
U261	MC + 10 v/o M_2C_3	98	316[e]	0.015	0.015	He	2590	34.1	———	
U262	MC + 10 v/o M_2C_3	98	INC-800	0.015	0.015	He	2590	34.1	———	

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

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

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

d. 20% cold-worked.

TABLE 463-XII

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 EBR-II Awaiting insertion into X156
U242	MC	93	304SS	None	0.015	1175	35.8	At EBR-II Awaiting insertion into X156
U243	MC	93	304SS	None	0.030	1150	33.8	At EBR-II Awaiting insertion into X156
U244	MC	93	304SS	None	0.015	1175	35.8	At EBR-II Awaiting insertion into X156
U245	MC	93	304SS	None	0.030	1150	33.8	At EBR-II Awaiting insertion into X156
U246	MC	93	316SS	None	0.015	1190	36.4	At EBR-II Awaiting insertion into X156
U247	MC	93	316SS	None	0.030	1150	33.8	At EBR-II Awaiting insertion into X156
U248	MC	93	316SS	None	0.030	1140	36.4	At EBR-II Awaiting insertion into X156
U249	MC	93	INC-800	None	0.015	1210	36.4	At EBR-II Awaiting insertion into X156
U250	MC	93	INC-800	None	0.030	1145	36.4	At EBR-II Awaiting insertion into X156
U251	MC	93	304SS	None	0.030	1145	36.4	At EBR-II Awaiting insertion into X156
U252	MC	93	304SS	Vanadium-slots	0.030	1140	36.4	At EBR-II Awaiting insertion into X156
U253	MC	93	304SS	Iron-slots	0.030	1145	33.8	At EBR-II Awaiting insertion into X156
U254	MC	93	304SS	304SS-slots	0.030	1140	33.8	At EBR-II Awaiting insertion into X156
U255	MC	93	304SS	304SS-holes	0.030			At EBR-II - Rejected W inclusion in bottom weld
U256	MC + 10 v/o M_2C_3	98	304SS	Vanadium-slots	0.030	1140	34.0	At EBR-II Awaiting insertion into X156
U257	MC + 10 v/o M_2C_3	98	INC-800	Tantalum-slots	0.030	1135	33.5	At EBR-II Awaiting insertion into X156
U258	MC + 10 v/o M_2C_3	98	304SS	304SS-slots	0.030	1145	33.5	At EBR-II Awaiting insertion into X156
U259	MC + 10 v/o M_2C_3	98	INC-800	304SS-slots	0.030	1150	34.6	At EBR-II Awaiting insertion into X156

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

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

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.

1. Series UL Tests

A cooperative effort has been carried out with Gulf United Nuclear Fuels Corporation in the area of TREAT testing. A series of four tests, designated LASL Series UL, will determine the effect of irradiation on the

TABLE 463-XIII

SERIES B-1 AND B-2 EBR-II NITRIDE IRRADIATION EXPERIMENTS[a]

Experiment No.	Fuel Density, % T.D.	Smear Density, % T.D.	Cladding Wall Thickness, in.	Max. Linear Power, kw/ft	Status
B-1-1	94.1	80.2	.020	27.9	X152 - In
B-1-2	93.9	80.6	.020	27.1	X152 - In
B-1-4	93.8	84.9	.020	29.0	Destructive Exam
B-2-1	94.7	81.6	.020	32.7	X152 - In
B-2-2	94.4	81.6	.020	32.6	X152 - In
B-2-3	94.0	81.0	.020	32.4	X152 - In
B-2-4	94.2	75.6	.015	32.4	Destructive Exam
B-2-6	94.0	81.6	.010	36.0	X152 - In
B-2-7	93.9	81.7	.010	36.7	X152 - In
B-2-8	93.8	81.6	.010	36.8	Destructive Exam at BMI

---

[a] All capsules are sodium bonded. Capsule cladding is 0.375 in. O.D. x 0.335 in. I.D. Type 304 stainless steel. Element cladding for the B-1 experiments is 0.290 in. O.D. Type 304 stainless steel. Element cladding for the Series B-2 experiments is 0.315 in. O.D. Type 316 stainless steel. The fuel is $(U_{0.8}Pu_{0.2})N$.

[b] Original sponsor - BMI.

TABLE 463-XIV

SERIES B-3 EBR-II NITRIDE IRRADIATION EXPERIMENTS[a,c]

Experiment No.	Fuel Density, % T.D.	Bond Type	Smear Density, % T.D.	Cladding Wall Thickness, in.	Max. Linear Power, kw/ft	Status
B-3-2	88.4	Na	82.8	0.016	37.7	X119B - In
B-3-3	91.2	Na	85.2	0.016	38.9	X119B - In
B-3-4	93.0	Na	86.4	0.016	38.9	X119B - In
B-3-5	90.4	Na	84.0	0.016	41.5	X119B - In
B-3-6	94.6	He[b]	88.8	0.020	34.2	X119B - In
B-3-7	88.5	He	87.9	0.020	34.2	X119B - In
B-3-8	89.8	He[b]	85.5	0.020	38.4	X119B - In

---

[a] Capsule claddings are Type 304 stainless steel, 0.375 in. O.D. x 0.335 in. I.D. Element claddings are 0.316 in. O.D.

[b] Pellets are annular with a 0.070 in. diameter hole.

[c] Original sponsor - BMI.

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

LASL will assume complete responsibility for these tests in fiscal year 1973. During the past fiscal year, LASL has had the responsibility for specifying the TREAT reactor test conditions and preparing the safety analysis and other documentation 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.

Gulf United has fabricated the fuel elements and inner capsules for the Series UL tests. The unirradiated elements (tests LASL-UL-1 and LASL-UL-2) have been assembled in the inner capsule. Inner capsules for the preirradiated elements have been fabricated by Gulf United, but assembly of the fuel elements into the inner capsules has not been performed. This assembly requires hot cell facilities.

Outer TREAT capsules, obtained from Oak Ridge National Laboratory, will be used in this series of tests to contain the inner capsules. Two TREAT capsules,

TABLE 463-XV

SERIES C-5 EBR-II NITRIDE IRRADIATION EXPERIMENTS[a]

Experiment No.	Fuel Density, % T.D.	Smear Density, % T.D.	Max. Fuel Temp. at Startup, °F (°C)[b]	Max. Clad Temp., °F (°C)[b]	Max. Linear Power, kw/ft[b]	Status
C-5-1	92.0	79.4	---	---	---	Reject; chips, air in plenum
C-5-2	93.3	79.4	---	---	---	Reject; chips, air in plenum
C-5-3	94.0	79.9	---	---	---	Reject; chips, air in plenum
C-5-4	95.1	80.9	2112 (1156)	1326 (719)	33.2	At LASL for NDT
C-5-5	95.4	81.6	SPARE			At LASL for NDT
C-5-6	93.3	79.3	2116 (1158)	1328 (720)	33.3	At LASL for NDT
C-5-7	94.4	80.5	2164 (1184)	1336 (724)	33.7	At LASL for NDT
C-5-8	94.3	74.4	2061 (1127)	1154 (623)	32.7	At LASL for NDT
C-5-9	94.2	80.2	2071 (1133)	1203 (651)	33.5	At LASL for NDT
C-5-10	94.1	80.2	2021 (1105)	1157 (625)	32.6	At LASL for NDT
C-5-11	93.9	80.6	2050 (1121)	1165 (629)	33.4	At LASL for NDT
C-5-12	94.2	74.1	2050 (1121)	1191 (644)	32.5	At LASL for NDT
C-5-13	95.5	75.2	2036 (1113)	1154 (623)	32.1	At LASL for NDT
C-5-14	95.7	75.4	2087 (1142)	1312 (711)	32.0	At LASL for NDT
C-5-15	95.2	75.4	2036 (1113)	1188 (642)	32.1	At LASL for NDT
C-5-16	95.6	75.4	SPARE			At LASL for NDT
C-5-17	95.7	75.5	---	---	---	Reject; leaked, air in plenum
C-5-18	93.9	79.6	2039 (1115)	1193 (645)	32.6	At LASL for NDT
C-5-19	93.6	78.9	2054 (1123)	1200 (649)	33.0	At LASL for NDT
C-5-20	94.7	80.6	2024 (1107)	1156 (624)	32.4	At LASL for NDT

---

[a] All elements are sodium bonded. The fuel is $(U_{0.8}Pu_{0.2})N$ pellets. The cladding is 20% cold-worked Type 316 stainless steel, 0.310 in. O.D. by 0.280 in. I.D.

[b] Recommendation of the original sponsor - BMI.

TABLE 463-XVI

SERIES O-NI EBR-II NITRIDE IRRADIATION EXPERIMENTS[a]

Experiment No.	Fuel Density, % T.D.	Smear Density, % T.D.	Temp. at Startup, °F (°C)[c]	Max. Clad Temp., °F (°C)[c]	Max. Linear Power, kw/ft[c]	Status
O-NI-1	89.9	77.7	2085 (1140)	1200 (649)	32.9	At LASL for NDT
O-NI-2	90.3	78.0	2043 (1117)	1325 (718)	33.1	At LASL for NDT[b]
O-NI-3	90.0	77.8	2128 (1164)	1323 (717)	32.6	At LASL for NDT
O-NI-4	89.6	77.4	2133 (1167)	1323 (717)	32.8	At LASL for NDT
O-NI-5	90.4	78.1	2068 (1131)	1160 (627)	32.9	At LASL for NDT[b]
O-NI-6	89.3	77.2	SPARE			At LASL for NDT[b]
O-NI-8	89.6	77.4	SPARE			At LASL for NDT

---

[a] All elements are sodium bonded. The fuel is $(U_{0.8}Pu_{0.2})N$ pellets. The cladding is 20% cold-worked, Type 316 stainless steel, 0.310 in. O.D. by 0.280 in. I.D.

[b] Elements O-NI-2, -5, and -6 have large fuel chips in the pellet-cladding annulus.

[c] Recommendation of the origin sponsor - ORNL.

TABLE 463-XVII

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

---

[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-XVIII

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.

presently at Gulf United, will be used to complete the assembly of tests 1 and 2, and will be reused for tests 3 and 4. During preliminary testing, Gulf United found leaks in an electrical seal in the TREAT capsule head on both capsules. This seal provides final high pressure containment in case of an accident. It is made by potting electrical wires into the head with epoxy resin. LASL has obtained spare TREAT capsule heads and the associated hardware from ORNL, and is presently preparing new seals.

Calculations for the safety analysis required for these tests have been performed. These calculations 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 to TREAT. The data package covering tests 1 and 2 was approved pending additional quality assurance information on the testing of the TREAT capsules after the electrical seal is completed. The data package for tests 3 and 4 (the pre-irradiated elements) was approved pending additional quality assurance information on the assembly of the fuel elements into the inner capsules and the final TREAT capsule tests.

The fuel elements, inner capsules and TREAT capsules for tests 1 and 2 are at Gulf United, awaiting shipment to LASL. The fuel elements for test 3 and 4 have completed irradiation in EBR-II and post-irradiation nondestructive examination at the LASL hot cell facilities; they are presently in storage at LASL. The inner capsules for tests 3 and 4 are at LASL.

2. 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, (P, Pu) C and (U, Pu) N fuels by defining failure thresholds and the types of failure experienced by these fuels. Table 463-XIX summarizes the test parameters and objectives. Approval-in-principle has been received from the AEC for this series of tests.

The two ORNL TREAT capsules being used for the Series UL tests will be modified at the end of that series to incorporate a thermal neutron filter. The fuel for Series 1 tests contains fully enriched uranium; without a thermal neutron filter, an edge to center power generation ratio of approximate 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:

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.[4]

Design work on the modifications to the TREAT capsule and design of the inner capsules for this series is in progress. TREAT capsule modifications require the fabrication of new heater can inserts containing the thermal neutron filter. Fabrication drawings are being made. The inner capsules for this series must be designed to incorporate a pressure transducer which will measure fuel element pressure during the transient. Manufacturers of pressure transducers have been reviewed, and a Kaman variable impedence transducer has been selected for use in tests 1 and 2 of this series. Fabrication drawings are being made for the inner capsules for these tests.

Preliminary neutronic calculations of the average energy calibration factor and edge to center power generation ratio for Series 1 have been made. These are presently being used in heat transfer calculations to determine the optimum reactor operating conditions to achieve the test results and to prepare a preliminary safety analysis.

III. FUEL PROPERTY MEASUREMENTS

A. Differential Thermal Analysis

(J. G. Reavis, R. Brewer)

The program of differential thermal analysis of irradiated UO_2-PuO_2 fuel materials supplied by GE-Sunnyvale is continuing. The data accumulated has been treated statistically to determine the accuracy of measurement of thermal arrest temperatures.

Corrections of temperatures measured using optical pyrometric techniques were made according to the equation

$$\frac{1}{T_c} = \frac{1}{T_o} + A$$

where T_c is the corrected temperature in deg. K

T_o is the observed temperature in deg. K

A is a constant,the value of which depends on light absorption by the optical system between the furnace and the pyrometer, A was evaluated by repeatedly observing T_o for melting and freezing of high purity standard samples of Pt, Rh and Ir 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 is $(65.03 \pm 0.18) \times 10^{-6}$ at the 95% confidence level. As an example, the confidence interval in this correction is ± 5° at a corrected temperature of 2500°C.

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

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

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

The average values of arrest temperatures observed for four capsules of UO_2-PuO_2 are listed in Table 463-XIX with the corresponding 95% confidence levels. The term "solidus" was not used in Table 463-XIX 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,[5] 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-XIX may not be the true liquidus temperatures, but are temperatures of beginning of macro-freezing of the samples.

TABLE 463-XIX

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

Sample	% PuO_2	O/M	No. of Cycles	Burnup, at.%	Arrest Temps, °C Heating	Arrest Temps, °C 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

With one exception, the confidence levels listed in Table 463-XIX are acceptably small. The large uncertainty in the heating arrest temperature listed for F3B-7C, sample 1 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 rather large difference between samples 1 and 2. While it is possible that there is some chemical difference between the samples, this seems to be a rather unlikely explanation.

Another unexpected observation in Table 463-XIX is the relation of arrest temperatures of samples A-1 and A-2. Based on U/Pu ratios alone,[6] 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,[7] the effect is not expected to be this large.

Other irradiated samples of UO_2-PuO_2 have been sealed in tungsten capsules and observed using DTA, but these capsules have leaked at temperatures above 2000°C. Good quality DTA curves were obtained below 2000°C, and

TABLE 463-XX

ESTIMATES OF HEATING ARREST TEMPERATURES OF IRRADIATED UO_2 - PuO_2 SAMPLES

Sample	PuO_2, %	Burnup, atom %	Heating Arrest Temp., °C
E1H-29A	25	7.6	~2755
E1H-29C	25	9.0	~2675
FOK-H	20	5.4	> 2710
F2X	20	9.7	~2660
F2G-K	20	10.0	~2625
F2G-E	20	10.6	~2670

no arrests were detected. Arrests were detected on heating above 2000°C, but large uncertainties in temperature measurement were caused by film deposition on the furnace window through which light was transmitted to the optical pyrometer. Estimates of heating arrest temperatures are listed in Table 463-XX. Although these temperatures have little or no significance individually, the group of observations may be taken as lending support to other observations[8] which indicate a lowering of the macro-melting point of UO_2-PuO_2 fuel materials by about 100° at 10 atomic per cent burnup.

After it was found that UO_2-PuO_2 irradiated to relatively high burnups consistently leaked from the sealed tungsten capsules at high temperatures, some of the welds were inspected. It appears that leakage was through microcracks in the welds. The effects of changing welding current, rate of travel, capsule geometry and addition of other metals to the weld have been investigated. The most promising technique appears to be addition of a thin Ta shim between the lid and the capsule body which acts as an alloy additive in the weld. This appears to reduce the grain size and cracking in the welded area. Isolated voids are observed in such welds, but they do not appear to open either to the inside or the outside of the capsule.

Other observations made on the irradiated UO_2-PuO_2 samples did not directly involve DTA, but did make use of samples subjected to DTA. These were observations of the appearance of samples after melting. The capsule containing sample F3B-7C-1 (UO_2-25% PuO_2, 4.3 atom % burnup), which had been taken through melting two times, was sawed longitudinally and viewed at a magnification of 10X. Sample F2X-K (UO_2 - 25% PuO_2, 9.7 atom % burnup), which had been cycled through melting six times and showed some evidence of leakage, was observed in the same manner. The appearance of these samples was not significantly different from that of unirradiated UO_2-PuO_2 melted in the same manner. Specifically, the molten oxide had formed a smooth concave meniscus at its surface. There was no evidence of a stable froth in the void space above the level of the molten oxide. This is in contradiction to behavior of a previous sample of irradiated UO_2-PuO_2, but the difference may be due to the high impurity content of the earlier sample.

B. High Temperature Calorimetry of Irradiated Oxides

(D. G. Clifton and R. Brewer)

High temperature drop calorimetric enthalpy measurements are reported here for irradiated and unirradiated samples of UO_2 - 20% PuO_2. The materials, obtained from the Nuclear Materials and Equipment Corporation (NUMEC), are considered to be representative of typical commercial grade LMFBR oxide fuels.

The calorimeter, installed in a LASL hot cell, and the experimental procedures have been previously described.[9]

Tables 463-XXI and 463-XXII list the recommended values obtained for the enthalpy measurements for the irradiated and unirradiated sample of UO_2 - 20% PuO_2, respectively. The irradiated sample, 40.006 gm, was taken from the NUMEC-B-9 fuel capsule[10] that had been irradiated in EBR-II to a burnup of 56,000 MWD/MTM(th), 6.2 at.%. The unirradiated specimen, 42.3345 gm, was made from equal amounts of archival UO_2 - 20% PuO_2 taken from two batches of material obtained from NUMEC designated Batch Run No. 12 and Batch Run No. 25; the same material mixture from which NUMEC-B-9 was fabricated.

The composition of the archival material is $U_{0.80}Pu_{0.20}O_{2.00}$; the O/M ratio was determined using the

TABLE 463-XXI

ENTHALPY MEASUREMENTS OF IRRADIATED

$U_{0.80}Pu_{0.20}O_{2.00}$

(NUMEC B-9-56)

T, °C	T, °K	H_T-H_{298}, cal/gm
1186	1459	87.4
1321	1594	102.6
1357	1630	103.0
1358	1631	102.5
1463	1736	112.5
1529	1802	117.8
1597	1870	125.0
1611	1884	126.8
1662	1935	131.1
1721	1994	136.3
1810	2083	144.5
1832	2105	149.5
1901	2174	152.5
1954	2227	155.4
1971	2244	160.9
1999	2272	162.6
2024	2297	166.0
2125	2398	177.7

TABLE 463-XXII

ENTHALPY MEASUREMENTS OF

ARCHIVAL $U_{0.80}Pu_{0.20}O_{2.00}$

T, °C	T, °K	H_T-H_{298}, cal/gm	H_T-H_{298}, cal/mole
1013	1286	69.9	18734
1237	1510	91.4	24496
1340	1613	98.5	26399
1500	1773	111.3	29830
1579	1852	120.3	32242
1712	1985	132.1	35404
1797	2070	139.5	37387
1875	2148	149.6	40094
1958	2231	158.0	42346
2078	2351	171.8	46044
2204	2477	180.9	48483

thermogravimetric method to be 2.00 and the metals composition came from direct analyses. The molecular weight of the archival material is 268.01 which corresponds to an isotopic composition of 91.4% enrichment in U^{235} for the uranium and 93.4% Pu^{239}, 6.1% Pu^{240} and 0.5% Pu^{241} for the plutonium.

The enthalpy values in Tables 463-XXI and 463-XXII are revised from those previously reported[9] and include some additional data. These newer values are recommended because of the more extensive experimental investigations reported below.

Another set of determinations of the self-heating of the irradiated sample were made about 1 year after the first set. The ratio of the specific powers of the sample at these two times was found to be 0.55 as compared with an approximated value of 0.61 that was obtained by interpolation of the energy release from the decay rate curves of fission products as calculated by Perkins and King.[12] The disagreement between these two ratios is consistent with the potential loss of some of the volatile fission products when the fuel capsule was opened. The enthalpy values for the irradiated sample in Table 463-XXI include self-heating corrections.

The revised enthalpy values in Tables 463-XXI. and 463-XXII are also based upon a calibration of the calorimeter with a National Bureau of Standards sample of Standard Reference Material 720, synthetic sapphire (Al_2O_3). Table 463-XXIII gives observed enthalpies for the standard Al_2O_3 as determined from the electrically evaluated energy equivalent of the calorimeter. These values are slightly revised from determinations previously reported because of recalculation of the window correction factors for the pyrometer, calibration of the pyrometer, and refinements of the electrical calibrations of the calorimeter. Included in Table 463-XXIII are the recommended NBS values and the percentage deviation of the observed values from the NBS data. The deviations suggest that a slight systematic error exists in the calorimetric observations based on the electrical calibration. Consequently, it has been decided to report the observed enthalpies of UO_2-PuO_2 based upon the Al_2O_3 standard rather than the electrical calibrations. Examination of the differences between the observed Al_2O_3 data and the

NBS data showed that a constant correction to the observed data of 1.4%, the average percentage deviation, gave good agreement. Therefore, this same correction factor was applied to all the UO_2 - 20% PuO_2 observations. Tables 463-XXI and 463-XXII list the corrected values referred to in the Al_2O_3 calibration.

Although the absolute data values have changed slightly, the earlier conclusion that the irradiated material has enthalpies 2 to 4% higher than the unirradiated material is still valid.

C. UO_2-PuO_2 Enthalpy Correlations

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

Several groups of investigators have made enthalpy measurements on unirradiated samples of solid solution UO_2-PuO_2. The compositions and temperature ranges considered in these studies are:

1. Gibby and Weber;[14] $U_{0.75}Pu_{0.25}O_{1.98}$; 296 to 1753°K.
2. Ogard and Leary;[15] $U_{0.802}Pu_{0.198}O_{2.00}$; 1168 to 2450°K.
3. Ogard and Leary;[15] $U_{0.802}Pu_{0.198}O_{1.98}$; 1176 to 2470°K.
4. Present work; $U_{0.80}Pu_{0.20}O_{2.00}$; 1286 to 2477°K.
5. Leibowitz, Fischer, and Chasanov;[16] $U_{0.8}Pu_{0.2}O_{1.97}$; 2348 to 3005°K.

Graphical comparison of all these data, 87 points from 298 to 3005°K, shows general agreement although there is more scatter in the data of Ogard and Leary and the present work than in the other two sets of data. However, considering that the data were acquired by four different calorimeter systems and that the materials are of different compositions, the overall comparison is good.

A joint effort is being undertaken by representatives of all the above investigators to obtain a "best" fit for the enthalpy curve versus temperature for the reported data and to generate a recommended heat capacity expression applicable from 298 to 3000°K. Because this general fit will ignore compositional differences such as variable ratios of U to Pu and O to M, the resulting expression will give, at best, approximate engineering values for the quantities.

To date, the data have been least squares fit to several polynomial functions of temperature applying the constraints that $(H_T - H_{298}) = 0$ at $T = 298°K$ and $C_{p298} = 15.45$ cal/deg. mole. No constraints were imposed upon the signs of the parameters. So far, the best functional representation obtained for the data is

$$H^0_T - H_{298} = -8.14781 \times 10^3 + 2.1621 \times 10^1 T - 5.30066 \times 10^{-4} T^2 + 1.78428 \times 10^{-10} T^4 + 5.21628 \times 10^5 T^{-1}.$$

All of the enthalpy values reported, with the exception of four data points, are reproduced within 3% using this equation. Heat capacity values calculated from the derivative of this expression are within 10% of both the calculated values reported by the individual investigators and the direct heat capacity measurements of Affortit and Marcon.[17]

The equation reported above should be regarded as preliminary. Further attempts are being made to construct functions that better represent the data and at the same time involve parameters that can be more easily interpreted physically.

TABLE 463-XXIII

ENTHALPIES OF Al_2O_3

T, °K	$H_T - H_{298}$, cal/mole obs.	NBS	Deviation, %
1298	35676	36298	- 1.7
1399	38919	39510	- 1.5
1484	41977	42212	- 0.6
1583	45464	45475	0.0
1674	47585	48330	- 1.5
1675	47412	48381	- 2.0
1778	50206	51766	- 3.0
1786	51052	52000	- 1.8
1874	54549	54855	- 0.6
1909	55294	56079	- 1.4

D. 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. The object of this work is to fit all the published UO_2 enthalpy data to one function over the temperature range from 298 K to the melting point.

UO_2 enthalpy data, measured by drop calorimetry, are available from 483 to 3107 K. A total of 105 enthalpy-temperature data points have been reported by five investigators,[18-22] while others have only reported a fit of their data as a function of temperature.[23] Even when data are reported, an investigator normally fits his data to some function of temperature over the range of the data, and reports the function as a representation of the enthalpy. Common functions include polynomials in temperature and inverse temperature.[18, 22] For use, the functions representing enthalpy as a function of temperature are often differentiated to obtain the heat capacity. A comparison of the heat capacity curves of different investigators in a temperature range where they overlap shows significant variations in the heat capacity and its derivative.[19, 22]

A number of functional forms were examined. The only constraint on form was that the function be smooth enough to provide a reasonable representation of the heat capacity when differentiated. 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.[24, 25] 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 $\Delta H(T)$ 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 $\Delta H(298)$ 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; $C_p(298) \equiv 15.2$ cal/mole K.[26] To accomplish this we have (neglecting $C_D(298)$).

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

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 experimentally the percentage error is constant. Table 463-XXIV shows the final values of the constants obtained. Figure 463-2 shows a plot of the enthalpy data as a function of temperature along with the calculated curve. Figure 463-3 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 evident from this plot. The maximum deviation of the data from the calculated curve was 2.7%. Figure 463-4 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.[25, 27, 28] None of these data was used in the least squares fit.

TABLE 463-XXIV

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	2.04×10^6

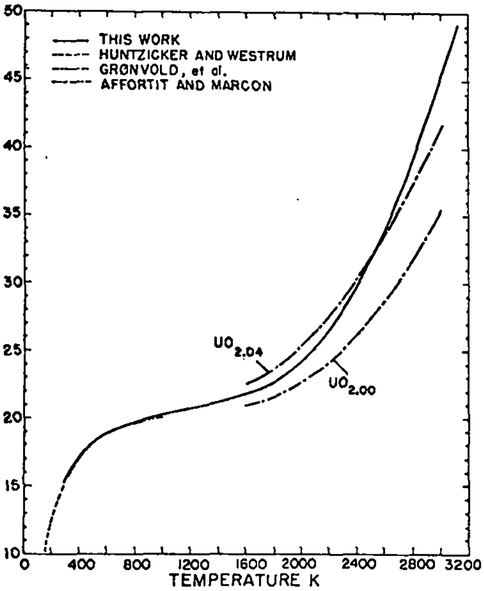

Fig. 463-2. Enthalpy of UO_2 as a function of temperature.

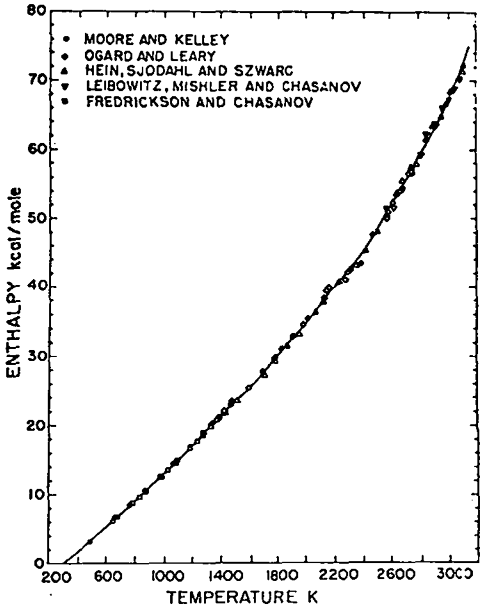

Fig. 463-3. Deviations and percentage deviations of measured enthalpy from calculated curve. Data point legend shown on Fig. 463-2.

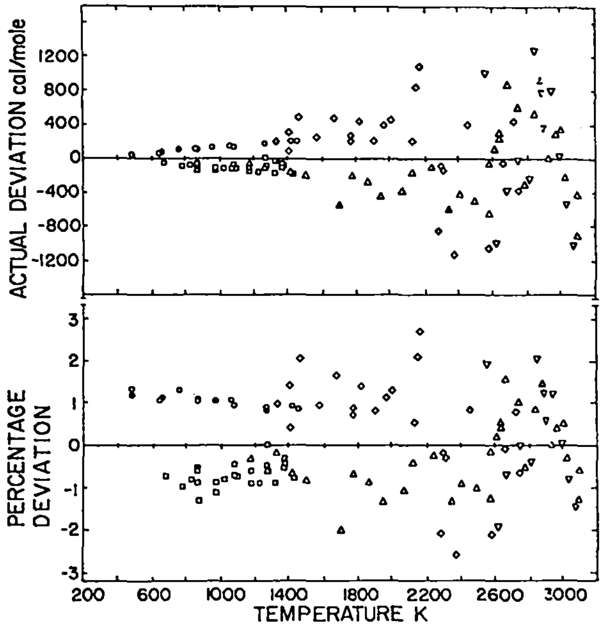

Fig. 463-4. Heat capacity of UO_2 as a function of temperature.

IV. QUALITY ASSURANCE

During the previous year a major emphasis has been placed on the development of a quality assurance system for the program. This system was constructed to specifically address the requirements of RDT standard F2-2T. A Quality Assurance Manager was appointed and given the responsibility for the preparation of the basic QA manual that governs the activities of all of the RDT projects. In the Plutonium Ceramic Fuels Program, a set of approximately 140 documents were prepared, approved, and put into effect for current experimental tasks. These documents define the planning, design, and fabrication of experiments and experimental assemblies by means of procedures, specifications, and descriptions covering all phases of the tests.

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PROJECT 472

ANALYTICAL STANDARDS FOR FAST BREEDER REACTOR OXIDE FUEL

Person in Charge: R. D. Baker
Principal Investigator: G. R. Waterbury

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 by the fuel vendors and the reactor operator for the above materials; (4) the preparation of continuously updated compilation 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; and (7) serve as a "neutral" referee laboratory, as may be required, to analyze samples in dispute between a vendor and a reactor operator. 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

(J. E. Rein, C. F. Metz, W. H. Ashley, R. T. Phelps, R. K. Zeigler, G. R. Waterbury)

A program equivalent to that in operation for the production of FFTF mixed oxide fuel is being established for the production of FFTF boron carbide pellets.

A. Status of Analytical Methods and Qualification of Analytical Laboratories

The first AEC-Internal Round Robin to evaluate methods for measuring seven HEDL-specified chemical properties of the boron carbide to be manufactured for the FFTF was completed in September 1971.(1) The participating laboratories were HEDL, ORNL, and LASL. Methods for the determination of total boron, total carbon, and isotopic boron were judged to be satisfactory. The methods for the determination of 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 samples were a powder blend of boron carbide containing added chloride and fluoride salts for the halogen method and batches of HEDL-supplied boron carbide pellets for the other three methods. The results for this round robin, completed in February 1972, showed that the four improved methods were satisfactory.

Copies of the seven analytical methods were distributed to the three potential vendors of FFTF boron carbide pellets by HEDL and a Vendor Round Robin was started in May 1972. In addition to the three vendors, HEDL and LASL are participating in this round robin. Completion is expected in late July 1972.

B. Preparation of Calibration Materials

An important factor controlling the accuracy of analytical methods is the use of proper calibration materials. In this program concerned with the production of a reactor material, the use of the same calibration materials by all the laboratories involved reduces between laboratory differences which, in turn, reduce vendor-reactor operator differences. Standards from NBS are available to calibrate methods for the determination of total boron and isotopic composition and are specified for use in this program. For most other methods, powder blends with a matrix of boron carbide will be prepared and characterized at LASL. The HEDL has supplied batches of boron carbide for this purpose which now are being extensively analyzed for base material contents of the various determined components prior to the preparation of the blends.

C. Preparation of Quality Control Samples

The most effective test of the accuracy and precision of the results being turned out by an analytical laboratory is a quality assurance program administered by an independent organization. During production periods of FFTF control rod absorber material, LASL-prepared quality control samples that match the manufactured material will be distributed to the vendors and to the HEDL laboratory by the HEDL quality assurance organization. The general rate of analysis of quality control samples is one per 8-h working shift.

The sampling plan for this quality control program has been prepared in cooperation with HEDL. A variety of boron carbide materials, including batches of pellets and powders, has been supplied by HEDL. These materials are now being chemically analyzed at LASL to establish the base concentration levels of the various components. The effort required to prepare quality control samples is large for two reasons: (1) extensive blending operations followed by samplings and chemical analyses are necessary to ensure that the blends have homogeneous distributions of the added trace components in the powder matrices, and (2) a relatively large number of blends is prepared because a new series of three blends is used each production quarter.

D. RDT Standard of Analytical Methods

Initial drafts of ten methods have been prepared for publication as RDT Standard F-11-2 as a joint HEDL-LASL effort. Final review of these methods, listed below, is in progress. The HEDL will submit the final draft to the AEC. The methods are for determination of:

1. Total Boron
2. Total Carbon
3. Boron Isotopic Composition
4. Soluble Boron
5. Soluble Carbon
6. Chloride
7. Fluoride
8. General Metallic Impurities
9. Gas Content
10. Water

E. RDT Standard for Qualification and Control of Analytical Laboratories

An initial draft of this document, prepared for publication as RDT Standard F 2-8 by LASL, has been reviewed jointly with HEDL. The final draft, to be submitted to the AEC, is now being prepared by HEDL.

This document prescribes the course of action by which analytical laboratories establish technical competence to analyze boron carbide chemically. It also provides a quality control program for the continual evaluation of the analytical data obtained during periods of boron carbide production.

F. Studies and Improvements of Analytical Methods

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

1. The Dissolution of Boron Carbide Materials: The classical dissolution of boron carbide by fusion with sodium carbonate has several disadvantages. The sample must be finely pulverized which causes some unavoidable contamination, relatively large amounts of the carbonate reagent are required, and mechanical losses are difficult to avoid in both the fusion step and in the subsequent neutralization of the excess carbonate. A limited investigation of the solubilization of B_4C by fusion with Na_2CO_3 indicated that heating the crucibles in a furnace at controlled temperature, rather than with a flame, and continued heating at 600°C to oxidize the B_4C before the temperature was raised to fuse the Na_2CO_3 improved the fusion. Remaining disadvantages of the fusion method are the contamination introduced by the required pulverization of the B_4C and the large amount of flux needed. Treatment with acids in a sealed fused silica tube at 300°C was effective in dissolving B_4C that had not been powdered. Of the various acids mixtures tried, nitric acid was the most effective and produced the lowest residual gas pressures. The resulting solution was suitable for immediate titration, or for purification treatment if that is necessary. Only SiO_2 contamination was introduced. Further work on this dissolution is planned.

2. Determination of Total Boron: The titration of B with 0.1$\underline{N}$ sodium hydroxide after adding mannitol is subject to interference from hydrolyzable metal ions. We found that solutions of pure H_3BO_3 which contained all of the specification impurities at their maximum concentrations were sufficiently purified by a cation exchange resin treatment to reduce the bias in the B determination to + 0.03% relative. This was accomplished by passing the solutions through a 4-in.-long column of Dowex 50 resin, and then boiling the effluent solutions to remove CO_2 before titrating the B. To improve the precision of the boron titration, 1$\underline{N}$ NaOH was added from a weight buret until near the endpoint. Then 0.1$\underline{N}$ NaOH was added from a small buret. The endpoint was detected potentiometrically, using a second derivative method. For sixteen titrations of H_3BO_3, the relative standard deviation was 0.012%. A layer of pentane excluded air very satisfactorily during the titration.

3. The Determination of Total Carbon: A LECO WR-12 Analyzer was used for measuring total C according to a recommended method for determining C in steel. Small amounts of Fe, Cu, and Sn were added to the sample which was then heated inductively in O_2. The CO_2 produced was isolated in a molecular sieve trap and finally determined by a thermal conductivity measurement. The method was shown to be reliable by analyzing NBS Silicon Carbide SRM 112 with complete recovery of the certified C content.

The classical combustion in O_2 at 1300°C was also found to be satisfactory for SiC standards when V_2O_5 was used as a flux. In this work the CO_2 was measured gravimetrically after absorption on Ascarite. This method provided an independent measurement of the total C, but it was rather slow for routine use. It was preferred to use B_4C instead of SiC as the reference standard, and this combustion method will be used in the characterization of B_4C for total C.

4. The Determination of Soluble B: Soluble B is expected to exist in B_4C as B_2O_3 and elemental B. These minor components are determined after selective dissolution of B_2O_3 in 0.1$\underline{M}$ HCl from one sample, and both B_2O_3 and B in 1.6$\underline{M}$ HNO_3 from a second sample. Mannitol is added to the solutions, and the dissolved B is titrated with 0.1$\underline{M}$ NaOH. The 0.1$\underline{M}$ HCl satisfactorily dissolves B_2O_3, the attack on the B_4C matrix is minimal, and the weak acid solution is readily purified by cation exchange. The HNO_3 extraction is less straightforward. The 1.6$\underline{M}$ reagent dissolves B and B_2O_3 but also attacks some B_4C matrices as evidenced by continuing evolution of CO_2 and by increases in the amount of B in the solution. The effect is most often observed with powder samples and is apparently reduced by sintering treatments. Our search for possible improvements included use of flame emission spectrophotometry for the final measurement of the B, thereby avoiding the interference of hydrolyzable species and the necessity of removing them. Adequate sensitivity was attained by measuring the B at 5476Å in a lean nitrous oxide-acetylene flame. To test this method,

solutions prepared from six pellets of impure B_4C were analyzed individually by flame emission spectrophotometry and also by ion exchange purification followed by NaOH titration. The results (Table 472-I) show that the method is encouraging, but further work is needed to complete the development.

TABLE 472-I

COMPARISON OF FLAME EMISSION AND TITRATION VALUES

	Titration*	Flame Emission
HCl-soluble B	0.49% s = 0.04%	0.46% s = 0.04%
HNO_3-soluble B	0.73% s = 0.07%	0.79% s = 0.07%

* s is one standard deviation

The use of a H_2O_2 solution, barely acidified with HNO_3, has been described by Kotlyar and Nazarchuk$^{(2)}$ as a substitute for 1.6$\underline{M}$ HNO_3. Any concentration of H_2O_2 stronger than 6%, with 10 drops of HNO_3 added per 100 ml, dissolved powdered B within 1 h. Crystalline B of 100-mesh fineness required only a little longer. A 10% solution of H_2O_2 containing HNO_3 and a standard digestion time of 2 h were used in preliminary studies. This reagent appears to have real merit. Experiments with a powdered B_4C material already known to be subject to attack by the 1.6$\underline{M}$ HNO_3 reagent showed that the dissolution of B_4C, measured as dissolved B in the solution, was only about 25% as great with the H_2O_2 reagent as with HNO_3.

It has also been observed that the measured soluble B is influenced by the particle size of the sample material. It was suspected that the higher results obtained on finer material was at least partly due to increased attack on the matrix. Parallel experiments with the HNO_3 and H_2O reagents were made on a B_4C material that had been sieved to obtain two fractions, 100 to 200 mesh and < 200 mesh. In HNO_3, 0.45% of the coarse sample dissolved and 0.87% of the fine sample. In the H_2O_2, for the same digestion time, the corresponding values were 0.40% and 0.57%. This work confirms that attack of the B_4C matrix contributes substantially to higher values obtained with finely powdered material, and it shows that the attack is less with H_2O_2 reagent. Advantages of the H_2O_2 reagent include shorter extraction time and reduced bias from B_4C dissolution.

5. <u>The Determination of Soluble Carbon:</u> The method for measuring soluble C relies on the greater vulnerability to oxidation by H_2CrO_4 of some unspecified forms of C than of the B_4C matrix. The C is oxidized to CO_2 which is purified and measured manometrically. There is always some attack on the B_4C, resulting in a positive bias. Careful attention to reagent concentration, temperature of digestion, time of treatment, pulverization of sample, and even the dimensions of the apparatus is required to obtain reproducible results.

One of the most serious sources of variation is the temperature of the digestion. In 1 h, digestion of a B_4C sample at $110^{\circ}C$ produced 15% more carbon dioxide than digestion at 100°. Variations in the duration of the digestion were of less consequence. At 100°, an increase in digestion time from 50 to 60 min increased the measured C by about 8%. A temperature of $99 \pm 1^{\circ}C$ for 1 h was recommended for the reaction. The fineness to which the B_4C was ground had a significant influence on the measured soluble C. Tests on two samples, one ground to pass a 100 mesh screen and one to pass a 200 mesh screen, showed that the measured soluble carbon was higher by 28% (relative) for the finer sample. We recommend that each sample be ground in its entirety to the required fineness and thoroughly mixed before withdrawing sample portions.

Studies of the behavior of B_4C in the H_2CrO_4 reagent as a function of time showed that the B_4C continued to dissolve after the first hour. During the second hour, about 25% more C dissolved, and another 10% during the third hour. By the end of the fourth or fifth hour, production of CO_2 reached a steady state, continuing without further change at least to the tenth hour. The ratio of the weights of boron and carbon in solution during the steady state period was close to the theoretical for B_4C.

The physical state of the "soluble" C as it is present in a B_4C matrix was found to be important. High purity carbon materials, having different sizes of graphite crystallites were heated with H_2CrO_4 under the conditions of this method. The most nearly amorphous material dissolved to the extent of 75% in 1 h at 100°C, 88% dissolved in 1 h at 110°C, and 92% dissolved in 1.5 h at 110°C. Longer treatment at that temperature did not increase the attack. At 130°, the attack was 97% complete in 1 h.

A sample of glassy carbon was 19% dissolved in 1 h at 100°C. In the mid-range of crystallite sizes, a needle coke was 42% dissolved in 1 h at 100°C, and an isotropic coke having the best-developed graphite crystallites was about 75% dissolved under these conditions.

The results of these studies emphasized the need for closely controlled conditions of analysis among all laboratories.

6. Emission Spectrographic Determination of Metal Impurities in B_4C: Various emission spectrographic methods were studied for the determination of metal impurities in boron carbide pellets. In one method, 20 mg of a mixture containing 1 part B_4C sample, 2.25 parts GeO_2, and 6.75 parts graphite powder is burned to completion in a dc arc. Results are obtained by visual comparison of analytical lines in the sample spectra with lines in the spectra of calibration materials on a previously prepared calibration plate.

Several improvements in this method were made at LASL, and the improved method is now specified in RDT Standard F 11-2. The improvements included:

1. The use of one set of calibration materials (standards) containing all the required impurity elements at concentrations graded generally according to the maximum average concentration impurity limits.
2. Addition of B_4C to the calibration materials in the same amount as in the sample mixtures.
3. Exposure of the set of calibration materials on each plate with samples.
4. Use of a grating spectrograph with a reciprocal linear dispersion of 5 Å/mm and a resolving power of 23,000 or greater.
5. Use of a center-post electrode to hold the charge.
6. Specification of the analytical lines.
7. Determination of elements present at greater than 25% of the specified limit by microphotometry.

The B_4C added to the calibration standards was purified by treatment with hydrofluoric and nitric acid mixture in a Teflon-lined bomb at 150°C. Impurity element concentrations were reduced to acceptable levels. The analysis of the B_4C starting material and of the purified B_4C are given in Table 472-II.

TABLE 472-II

PURIFICATION OF B_4C IN A TEFLON-LINED BOMB

Element	Concentration of impurity element, µg/g Starting material	Purified B_4C
Al	150	50
Bi	< 25	< 25
Ca	80	30
Co	< 50	< 50
Cr	< 100	< 100
Cu	10	< 10
Fe	700	< 200
Mg	20	< 20
Mn	< 20	< 20
Ni	< 40	< 40
Si	800	200
Ti	< 50	< 50
V	< 40	< 40
Zr	< 200	40

Calibration materials, prepared at LASL for the determination of metal impurities in B_4C, were used at HEDL and ORNL in round robin exchanges and will be used by vendors in the production of B_4C. The calibration blends contain the required buffer mixture (GeO_2 and graphite powder), and the impurity element at eight concentration levels.

The precision of the results obtained at LASL was shown from four determinations on each of six pellets. The relative standard deviations ranged from 3.2 to 5.5% for ten specification elements.

In an alternative method, samples and standards are treated chemically to make them similar. The method is a Na_2CO_3 fusion of B_4C, with subsequent conversion of the excess Na_2CO_3 to NaCl by adding HCl. The dried salts are mixed with graphite powder for spectrographic analysis. Four B_4C samples have been analyzed by this fusion method. Analytical results obtained were compared to results by the GeO_2-graphite buffer method. The Al determined by the fusion method was considerably higher in all four samples, Cr was slightly higher, Ca was equal or higher, Mn was essentially equal, and Fe, Ni, Si, Ti, V, and Zr were lower or equal. No explanation was found for the different results by the two methods. Because of the doubt in the buffer method due to differences between the standard and sample materials, the fusion method was considered to yield values closer to the true value.

III. ANALYTICAL CHEMISTRY PROGRAM FOR FBR MIXED OXIDE FUEL

(J. E. Rein, R. K. Zeigler, G. M. Matlack, W. H. Ashley, R. T. Phelps, G. R. Waterbury)

A. Qualification of Analytical Laboratories

The draft of the RDT Standard F 2-6 "Qualification and Control of Analytical Chemistry Laboratories for Mixed Oxide Fuel Analysis" was revised in April 1972 jointly by HEDL and LASL. This draft, to be submitted to the AEC by HEDL, presents requirements for qualification of analytical laboratories to analyze chemically the mixed oxide fuel and source materials, and describes the quality control program that will be in effect in analytical laboratories during periods of fuel production. A requirement for qualification is that a laboratory satisfactorily analyze a series of test samples for twenty specifications prior to the start of fuel production. These test samples were provided to HEDL along with associated acceptance limits for the various specifications and are now being analyzed by the two potential fuel vendors.

B. Calibration Materials and Quality Control Samples

Calibration and quality control materials, prepared from powder blends of metal and nonmetal impurities in matrices of $(U,Pu)O_2$, UO_2, and PuO_2, were extensively sampled and analyzed. Batches of sintered $(U,Pu)O_2$ pellets were carefully characterized for total and isotopic U and Pu contents, homogeneity, and O/M ratios.

These materials were distributed by HEDL and are now in use in the vendor and HEDL analytical laboratories. The addition of the vendor for the ceramic grade PuO_2, a heavy usage of calibration materials by the fuel vendors, and the need for new series of quality control samples at 3-month intervals are resulting in a larger effort than planned at LASL in preparing materials. This expanded effort has a high priority because of its relationship to the FFTF operation. Effort on research and development in this program, therefore, must be delayed.

C. RDT Standard of Analytical Methods

Jointly with HEDL, a draft of RDT Standard F 11-1 "Analytical Chemistry Methods for Mixed Oxide Fuel" was prepared. HEDL will submit this draft to the AEC. This document contains twenty four methods for the analysis of the fuel and the source U and Pu materials.

D. Quality Assurance Sampling - Chemical Analysis Plan

A statistical sampling and chemical analysis plan developed for FBR $(U,Pu)O_2$ fuel pellet production, provides an economic incentive to a fuel vendor to produce high quality fuel. The incentive is a reduction in sampling and analyses required as the precisions of the chemical analysis methods and the quality of the product improve.

A paper describing this plan is being prepared for publication.

E. Development of Analytical Methods

1. Determination of Burnup

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

A sequential chemical separation-mass spectrometer method for the burnup measurement of FBR fuels was improved. In the original method, the Nd, Pu, and U were separated from the sample and from each other and then measured individually in the mass spectrometer. Mass spectrometer operating conditions were subsequently developed to analyze Pu and U loaded together on a single filament. The separation method, therefore, was simplified and shortened. A second improvement was the substitution of disposable, inexpensive plastic ion exchange columns for previously used custom-fabricated glass columns.

The development of wet chemical and analytical methods using inexpensive apparatus has been initiated for burnup analysis of FBR fuels to achieve economy for large sample loads where decreased reliabilities are acceptable. The first system selected for study is a sequential separation of U, Pu, and total rare earths followed by spectrophotometric or microtitrimetric measurements.

A final draft of a document that encompasses all aspects of burnup measurement based on chemical methods of analysis and gamma-ray scanning has been completed. This document has been prepared jointly with the Allied Chemical Corporation (at the NRTS) and with the Argonne National Laboratory to provide a critical evaluation of burnup measurement techniques. A cooperative research and development program is under way in the three laboratories to obtain improved methods.

2. Determination of O/M Atom Ratios

(J. W. Dahlby and T. K. Marshall)

The O/M atom ratio of $(U,Pu)O_2$ fuel is determined in one recommended method from the weight change upon oxidizing the sample in air and then reducing it in dry Ar or He containing 6% H_2 at 1000°C. This treatment reportedly converts the sample to the stoichiometric dioxide. In an effort to understand better the conditions under which the stoichiometric $(U,Pu)O_2$ is produced, two experiments were conducted: The first measured the H_2O in the dry reducing gas, and the second determined relative reaction rates of the reduction.

The reducing gas is dried by $Mg(ClO_2)_2$ in a 2 in. by 6 in. drying tower. The residual H_2O was measured by a H_2O sensitive meter in the gas entering the reaction furnace; this gas contained < 1 ppm of water. When the Ar-H_2 gas was heated to 1000°C in the reaction furnace with no $(U-Pu)O_2$ sample present, the H_2O of the exhaust gas slowly increased to 2-3 ppm over a 6 h period. This small slow increase in indicated H_2O content had three possible sources: O_2 in the gas which reacts with the H_2 at elevated temperatures, O_2 in the metal tubing leading to the meter which reacts with H_2, and a sensitivity of the cell in the meter to H_2. The last possibility seemed most likely.

To determine at what relative rate the reduction reaction between the H_2 gas and the $(U-Pu)O_2$ took place, the exhaust gas was monitored while a 5-g sample of $(U-Pu)O_2$ was reduced to the stoichiometric dioxide. Less than 1 min after the H_2 was added, the H_2O content increased very rapidly to > 1000 ppm and remained there for over 11 min. After 12 min, the H_2O content of the gas decreased swiftly to 400 ppm, after 13 min to 240 ppm, and after 14 min to 180 ppm. The water content of the gas then decreased at a slower rate to 46 ppm in 1 h and 2 ppm in 7 h. By far most of the reaction took place during the first 15 min. The slowly decreasing rate of the indicated H_2O content in the exhaust gas after this time may be caused by small amounts of unreacted sample taking longer to react quantitatively, or by a slow "recovery" rate of the H_2O sensor cell after being exposed to large amounts of H_2O.

The determination of O/M ratios in mixed oxide fuels was further investigated by comparing results obtained by LASL with results obtained by HEDL on similar samples of sintered $(UPu)O_2$ pellets. To eliminate any bias caused by samples having been stored or treated differently, personnel at HEDL randomly chose 40 pellets from a batch which had been previously analyzed and determined to be homogeneous and consistent in O/M ratio. Twenty of the pellets were put in a shipping container and sent to LASL while the other twenty were put in another shipping container and stored at HEDL. Each of the shipping containers was opened on the same day and the O/M ratio was determined as quickly as possible by each laboratory.

In the method used by LASL, the sample was dried in Ar at 120°C, oxidized in air at 1000°C, and finally reduced to the stoichiometric dioxide at 1000°C in Ar-6% H_2. In the method used by HEDL, the sample was heated to 800°C in Ar-8% H_2 containing 4 mm partial pressure of H_2O. The average value obtained at LASL for the O/M ratio on eight samples containing 3 g each of crushed $(U-Pu)O_2$ sintered pellets was 1.964 ± 0.002, which compared well with the average obtained at HEDL of 0.961 ± 0.004. It was concluded that either method gave the correct results for O/M ratio on sintered $(U-Pu)O_2$ pellets.

It was previously shown that for unsintered reference material made from high purity U and Pu metal, reduction in dry Ar-6% H_2 obtained the correct results. This work was repeated using oxides prepared from the pure metals. The O/M ratios of the oxides produced by heating in dry Ar-6% H_2 averaged 2.003 ± 0.001 as compared to 2.037 ± 0.004 for oxides produced in Ar-6% H_2-4 mm H_2O vapor pressure. These results agreed with values obtained previously.

IV. PUBLICATIONS

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2. R. K. Zeigler, G. M. Matlack, J. E. Rein, C. F. Metz, "A Statistically Designed Program for Sampling and Chemical Analysis of Reactor Fuel Materials," Symposium on the Analytical Chemistry of the Nuclear Fuel Cycle, IAEA, November 28-December 2, 1971.

3. R. M. Abernathey, G. M. Matlack. J. E. Rein, "Sequential Ion Exchange Separation and Mass Spectrometric Determination of ^{148}Nd, Uranium, and Plutonium in Mixed Oxide Fuels for Burnup and Isotopic Distribution Measurements," Symposium on the Analytical Chemistry of the Nuclear Fuel Cycle, IAEA, November 28-December 2, 1971.

4. W. J. Maeck, R. P. Larsen, J. E. Rein, "Burnup Determination for Fast Reactor Fuels-A Review and Status of the Nuclear Data and Analytical Chemistry Methodology Requirements," AEC Report in press.

5. C. F. Metz, G. R. Waterbury, J. W. Dahlby, "The Measurement of Oxygen to Heavy-Metal Atom Ratio in Unirradiated Mixed Oxide Fuel," Symposium on the Analytical Chemistry of the Nuclear Fuel Cycle, IAEA, Vienna, November 28-December 2, 1971.

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2. E. E. Kotlyar and T. N. Nazarchuk, Zh. Anal. Khim., 15, 207, 1960.