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A PROGRESS REPORT

Quarterly Status Report on the
Advanced Plutonium Fuels Program

October 1 to December 31, 1971

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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LA-4595-MS	LA-4749-MS

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A Progress Report
UC-80 and
FAST REACTOR REPORT
SPECIAL DISTRIBUTION

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Advanced Plutonium Fuels Program

October 1 to December 31, 1971

Compiled by

R. D. Baker

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PROJECT 401

EXAMINATION OF FAST REACTOR FUELS

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

I. INTRODUCTION

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

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

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

II. EQUIPMENT DEVELOPMENT

A. Inert Atmosphere Systems

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

1. Disassembly Cell

The atmosphere was purified during the report period by a recirculating system which maintained impurity levels at 3 to 15 ppm O_2 and 1 to 5 ppm H_2O. The cell was placed on an Ar once-through purge for the week end of December 4 during a scheduled power outage. The concentrations of impurities were less than 25 ppm O_2 and 5 ppm O_2 during the outage.

2. Metallography Cells

The atmosphere was maintained in the two metallography cells by an Ar once-through purge pending installation of the butyl acetate removal system and replacement of the KBM oxygen catalyst tanks. Typical impurity levels have been reduced during the report period from maxima of 650 ppm O_2 and 50 ppm H_2O to 50 ppm O_2 and 15 ppm H_2O.

An experimental PVC manipulator boot with a polyurethane exterior coating was supplied by a Plastics Group at LASL. The boot was installed on December 1 in an effort to determine the resistance to the butyl acetate vapors present in the metallography cells. An exposure of at least three or four months will be required to determine the efficacy of the coating.

A study was made of the feasibility of converting the dry inert atmosphere in the metallography cells to a dry air atmosphere. If the recirculating purifier systems were used for the control of the H_2O concentration, very little additional effort or cost would be required to also maintain a low concentration of O_2. The use of air for the makeup gas for the alpha hox pressure differential control system would not be satisfactory as it would quickly saturate the purifier with moisture. Converting from an Ar atmosphere to one of N_2 would be feasible, although a somewhat higher level of moisture would be present in the cell due to higher levels of moisture in the N_2 supply gas. The lower price for N_2 would result in a 70-80% reduction in costs for the present makeup gas. Similar savings would be obtained by converting from an Ar once-through purge to a N_2 purge. No changes would be required in the design or operation of the inert cells due to the conversion to N_2.

B. Master-Slave Manipulator Maintenance

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

The establishment of a routine inspection and maintenance program appears necessary to assure that the master-slave manipulators provide continuing service. The frequency of breakdowns has been steadily increasing since the curtailment of manipulator maintenance and repair by specialized personnel. Certain operating personnel have recently been designated to develop experience in this area since 22 pairs of manipulator arms (3 different types) are in constant service, and 8 pair are available as spares.

A list of repair parts required to maintain the new CRL Model "L" MSMs was prepared for procurement.

C. Shipping Casks

The second cask (DOT SP-5885) for off-site shipping of 40-inch-long fuel pins was received in mid-November.

The small cask, designed to ship small sections of fuel pins off-site, will be available by about February 1, 1972.

A request was initiated recently to use a third "Rover-type" cask for the LASL operations. A survey of the operations indicates that the two casks currently on hand satisfy only the storage requirements at the Wing 9 Facility and the transfer between the DP West and Wing 9 facilities; the third cask would be available for off-site shipping.

The difficulties encountered with a contaminated Rover cask being shipped from Idaho to Hanford resulted in the temporary withdrawal of the DOT approval of these casks. Minor design corrections have been submitted for approval to DOT through the AEC Albuquerque Operations Office. It is hoped to have the casks reinstated to service by about February 10. LASL will be responsible for making the necessary corrections to the casks as required.

D. New Metallograph Blister

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

The alpha containment box and modular shield components were sand blasted and painted. The 14-in.-thick modules were filled with Pb shot and the 9 in.-thick ones with Pb bricks.

A final test set-up is being made, and appropriate coupling plates have been attached to insure proper orientation during re-assembly. The new Mini-Manipulators were installed and checked out for operations and coverage. A modification was made to the light well to render it essentially flush with the top of the box. Items remaining to be completed are:

1. Shop fabrication of the new gate valve connecting the box to the tunnel system.
2. Detailed design and fabrication of shield door for the bag-out port in the old metallograph shield module.
3. Shop fabrication of a new telescoping type mechanism for the bag-out port.

It is expected that these three items will be completed by February 1.

E. New Mechanical Profilometer

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

An equipment search is being made to find a 4-jaw scroll type chuck which will meet the precision requirements of the new profilometer design. The diameter sensing units (LVDT's) will be mounted on the jaws of the chuck. This profilometer will be used as a back-up unit and also for obtaining diameters of breached pins.

F. Butyl Acetate Removal System

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

Design, fabrication, and procurement of

components for the equipment to remove butyl acetate (used in metallography operations) from the inert gas systems are proceeding.

G. High Pressure Metallographic Sample Potting System

(C. D. Montgomery, T. Romanik, D. S. Shaffer)

Fabrication of a prototype pressure potting vessel was completed. The vessel was hydrostatically tested to 5200 psi. The test set-up, which has been approved by a responsible LASL Safety Engineer, is in use in beta-gamma cells. The samples prepared thus far have given encouraging results.

H. Cask Insert Elevator

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

Fabrication, assembly, and check-out of a 200-lb-capacity electro-mechanical elevator for use in the Rover type shipping casks have been completed. This remotely operated device has improved the transfer operations considerably.

I. Bausch & Lomb Optical Read-out Gauge

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

A new design for modification of the B and L gauge has been completed and submitted to the shope for fabrication. This design incorporates a system for adjusting the position of even a severely bowed fuel element so that its axis is perpendicular to the measuring anvils at the point of measurement. It is hoped that this improvement will permit the safe use of this equipment on badly bowed pins.

J. Radiography Cask

A preliminary study has been made of the requirements for a new radiography cask capable of handling fuel pins up to 61 in. long and with burnups as high as 10 at.%. It is proposed that depleted uranium be used for shielding. Additional shielding would be provided to accommodate the fueled section of the pin.

Since the cask will be 8 in. higher than the one currently in use, a hole will be drilled in the Betatron room in front of the machine to provide for the increased height. This increased height will pose no special handling problems at the two hot cell facilities or with the existing truck.

Detail design of the final system is expected to begin about the middle of January.

K. Scanning Electron Microscopy

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

The shielded transport cask and sample holder for irradiated samples have been fabricated and are now being checked. In addition, specimen procedures and shielding for the electron microscope are being developed.

L. Microstructural Analysis Equipment and Developments

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

1. The prototype ion gun etcher has been fabricated, assembled, and is in operation. Operating parameters for the best metallographic etching of materials are being determined.
2. A computer code IMAGE VI has been written and made fully operational. This code is on permfile and can be easily used from our remote terminal. This data reduction and interpretation code for image analysis contains plotting routines for our output which can also be used at our remote terminal.
3. The prototype high pressure impregnation system is being fabricated. Components for in-cell system are being procured.
4. The new electric stage for the B and L remote metallograph is being shipped to LASL.
5. Installation engineering drawings for the high speed photographic printer are in process.
6. A jet washer for in-cell metallographic speciment is being designed.
7. The theoretical study on the measurement of randomly shaped volumes in space is continuing. Preliminary results indicate that significant applications to microstructural image analysis will result from this study.
8. Upgrading electronics have been ordered for both the SEM and the SEM-EDX units.
9. Pattern recognition modules have been ordered for the Image Analysis Computers.

III. HOT CELL FACILITY AT DP WEST

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

A. Structure and Equipment

Enclosure of the balcony has been completed, and the air conditioning equipment has been moved into place. The plumbing and electrical work will be completed when craftsmen are available.

B. Hot Cell Equipment

1. Gamma Scanning Equipment

All of the lead-tungsten collimators have been poured and radiographed; seven of the eight units have been acceptable. The eighth unit was poured when potentially troublesome voids were observed. This last unit has been recently submitted for radiography. Installation of gamma scanning equipment in the cells will start in January.

2. Electro-Optical Profilometer

The periscope shielding has been designed and fabrication started.

A design has been submitted for a series of profilometer standards which should cover a wide range of fuel element diameters. Safety switches are presently being added to the mechanical stage to prevent damage in case of operator error.

3. Macro-Camera System

The Macro-Camera system has been installed, and the electrical wiring of this system is now being completed. Due to limited space at the face of this cell the camera stand is being modified to allow easy removal and precise replacement.

4. Pulsed Eddy Current Scanner

Components for the vertical drive mechanism for this device have been procured. A suitable four channel recorder with amplifiers and pre-amplifiers has been ordered.

IV. METHODS OF ANALYSIS

A. Measurement of U and Pu

(J. W. Dahlby, C. S. MacDougall, G. R. Waterbury)

Measurement of U and Pu without chemical separation by controlled potential coulometry is satisfactory for fuels having undergone as much as 6 at.% burnup. The Pu content is obtained from the integrated current required to either oxidize Pu(III) to (IV), or to reduce Pu(IV) to (III) at a Pt electrode. The U content is calculated from the net integrated current required to reduce U(VI) to (IV) at a Hg electrode. At burnups above 6 at.% the direct coulometric titrations are not sufficiently precise because of side reactions caused by the extremely high radioactivity of the large quantities of fission product elements. For this reason, methods are being investigated for quantitatively separating U and Pu from these fission products.

Initial effort was devoted to precipitation separations because of their simplicity, speed, and minimal requirements for manipulations, It was found that precipitation of some fission products as insoluble fluorides while U and Pu were oxidized to their soluble (VI) oxidation states greatly reduced the radioactivity, and the recoveries of U and Pu were no less than 99.8%. To complete the removal of fission products, the Pu and U were then reduced to their (III) and (IV) oxidation states, respectively, and precipitated as insoluble fluorides, leaving the fluoride-soluble fission products in solution. Satisfactory recovery of Pu resulted, but about 1% of the U was lost. As a 99% recovery was not considered adequate, hydroxide precipitation was tried for separating the U. First the U was precipitated in the absence of complexing agents to separate it from hydroxide-soluble fission products. Less than 0.1% of the U was lost in this step. To improve the separation factor, selective precipitation of the hydroxide-insoluble fission product elements while U(VI) is complexed with carbonate is now being studied.

B. Determination of C and H

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

Carbon and H are impurities that affect the irradiation behavior and the effective reactor lifetimes of cladding and fuel materials. Reliable measurements of these elements, therefore, are necessary in evaluating these effects. One well-tested determination of C and H consists of burning the sample in pure O_2 at 1000°C to convert these impurities to CO_2 and H_2O which are trapped and weighed. Equipment previously installed in a hot cell for these measurements was tested initially by analyzing standard samples containing known percent amounts of C and H. Recoveries of C and H were approximately 100%, and the relative standard deviation of a single measurement was 2%.

Further tests consisted of analyses of five different stainless steel claddings from fuel pins having undergone 3 to 8 at.% burnup. The results ranged from < 70 ppm to 1600 ppm for C and < 28 to 230 ppm for H. Then three mixed oxide fuels from the same fuel pins were analyzed with results ranging between < 20 and 370 ppm for C and < 10 to 153 ppm for H. The precision (1 σ) of repeated measurements on each fuel or cladding sample was within the expected limits of the method (± 10 ppm or ± 2%, whichever is larger).

Analyses of PuC and (UPu)C for C and H are planned to evaluate the method for measuring C at contents of approximately 5%. Modifications of a LECO Low Carbon Analyzer for hot cell use are in process to provide additional capabilities and higher temperature combustions.

C. Gamma Scanning

(J. R. Phillips)

The quantitative determination of gamma-emitting fission products is dependent on detector efficiency which must be measured as a function of gamma-ray energy. An energy calibration of one detector was completed using two sets of IAEA standards. The detector's efficiency increased exponentially in the energy range from 2 MeV to about 122 KeV where an anomalous reduction in the efficiency occurred. As the standards do not have gamma-rays in this energy range, a ^{75}Se source with gamma energies of 97 KeV, 121 KeV, 136 KeV, 265 KeV, 280 KeV, and 401 KeV was used. The peak areas were normalized to superimpose on the calibration curve in an attampt to obtain additional data points. The results indicated that the published values for the decay yields of ^{75}Se are incorrect. Other sources are being sought to complete the calibration of the detector.

A computer code, COLLIM, was developed to simulate the beam shaping by various collimator systems, and the calculated beam shapings for several systems were compared to the experimentally determined beam shapes. The calculated beam shape compares favorably with the experimental result for a 0.500-in. collimating slit. The results for the 0.020-in. collimator are difficult to interpret because significant mechanical distortions were introduced in the collimator during the fabrication process. The COLLIM code will be used to evaluate the collimators being fabricated for installation at DP site. Various parameters in the code will be changed to determine the optimum collimator design.

V. REQUESTS FROM DRDT

A. Examination of Unirradiated Fuels

(C. W. Bjorklund, E. A. Hakkila, K. A. Johnson)

Westinghouse ARD: Electron microprobe, x-ray, and optical microscopy examinations have been completed on ten samples from WARD, and the final report is in preparation.

B. Examination of Irradiated Material

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

General Electric Company: Melting point determinations of the irradiated mixed oxide fuel specimens are being performed. Details of the examination are reported under the Project 463 "Fuel Properties" section of this report.

Some cladding sections from these specimens are being prepared for oxygen and carbon measurements using equipment in the hot cells.

Gulf United Nuclear Fuels Corporation: Tests performed on Gulf United materials are described below.

Gamma scanning was applied to the non-destructive examination of the six following fuel pins shown in the table on the following page.

TABLE 401-I

POSTIRRADIATION EXAMINATION OF CAPSULES FROM GULF UNITED

	Examination	UNC Capsule Identity
1.	Micrometer Measurement	192. 197. 198. 200. 206. 208
2.	Radiography	195. 197. 198. 200. 206. 208
3.	Photography (Full Length)	187. 189. 191. 192, 194, 195 197. 198. 200. 206. 208
4.	Cover Gas Sampling	187. 189. 191. 192. 194. 195 197. 198. 200. 206. 208
5.	Cover Gas Analysis	187. 189. 191. 192. 194. 195, 197. 198. 200, 206. 208
6.	Na and Clad Removal[a]	187. 189. 191. 192. 195. 197. 198. 206, 208

[a] Na melting and clad removal on UNC-194 and -200 will be performed in an inert atmosphere. Cover gas analysis indicated that these two pins are breached.

TABLE 401-II

POSTIRRADIATION EXAMINATION OF PINS FROM GULF UNITED

	Examination	UNC Pin Identity
1.	Micrometer Measurements	138, 146
2.	Center Point Balance	138, 146
3.	Photography (Incremental)[a]	138, 146, 187. 180. 191. 192. 195. 197. 198. 206. 208
4.	Fission Gas Sampling	109, 111, 112
5.	Fission Gas Analysis	109. 111, 112
6.	Sectioning	107. 108. 109. 111, 112

[a] Photography of the breached UNC-194 and -200 pins will be performed in an inert atmosphere box following removal of the capsule cladding.

TABLE 401-III

GAMMA SCANS OF UNC FUEL PINS

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

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).

A cross section sample from UNC-219, which contained a U-Pu carbide fuel and had exceeded its melting point in places, was examined using the shielded electron microprobe.

Flux monitor wires from UNC-96, -99, and -104, were analyzed radiochemically for ^{54}Mn.

Microstructural examinations have been completed on five specimens, each, from UNC-92, -96, -99, and -104. The examinations in argon atmosphere included macrophotography, alpha and beta-gamma autoradiography and optical microscopy (including mosaics).

Microstructural examinations are in progress on UNC-107, -108, -109, -111, and -112.

Four specimens were prepared for the shielded electron microprobe. This included pre- and post-EMX photomicroscopy.

Nuclear Materials and Equipment Corporation: Examinations made on NUMEC materials are described in Table 401-IV.

Four gross gamma scans and one completed spectral scan were made on NUMEC-A-1 to determine which end of the fuel pin contained UO_2 pellets and which end contained UO_2-PuO_2 pellets.

Special optical microscopy was completed on several samples from A-10 and A-11.

Four samples were prepared for the shielded electron microprobe. This included pre- and post-EMX photomicroscopy.

Cross section samples of NUMEC-A-10A, NUMEC-A-10H, NUMEC-A-11F, and NUMEC-B-11 were examined with the shielded electron microprobe.

Burnup analysis was performed on one sample from NUMEC A-5.

A 2-inch section of NUMEC pin A-1 containing the UO_2-$(UPu)O_2$ interface was shipped to ANL on November 3, 1971. On November 10, 1971, twelve sections of fuel-cladding and 3 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.

WADCO Corporation: Two pins from the PNL series were received on December 2, 1971 from WADCO. Examinations made on these two pins during this period are tabulated in Table 401-V.

TABLE 401-IV

POSTIRRADIATION EXAMINATION OF NUMEC MATERIAL

	Examination	NUMEC Pin Identity
1.	Fission Gas Sampling	A-1, A-6
2.	Fission Gas Analysis	A-1. A-6
3.	Sectioning	A-1, A-6, A-10

TABLE 401-V

POSTIRRADIATION EXAMINATION OF WADCO MATERIAL

	Examination	PNL Pin Identity
1.	Visual Inspection	17-7, 17-33
2.	Preliminary Measurement	17-7, 17-33
3.	Photography (Full Length)	17-7, 17-33
4.	Radiography	17-7, 17-33
5.	Gamma Scanning	17-7[a], 17-33[b]
6.	Removal of Wire Wrap	17-33
7.	Photography (Incremental)	17-7, 17-33

[a] 4 gross and 1 complete spectral analysis

[b] 4 gross and 3 complete spectral analyses

The fission gas sampling and profilometry tests will be completed by January 15, at which time a sectioning diagram will be prepared by WADCO to designate the samples for destructive examination.

Material from Other Experimenters

Additional discussions have been held with GE personnel relative to the examinations to be performed on 5 pins to be shipped to LASL in January 1972.

Plans have been made to provide the cask for bringing the ORNL pin, irradiated in ETR, to LASL for examination in February or March. Details of the examination and priority scheduling are yet to be discussed with DRDT and ORNL.

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. Fuel Synthesis and Fabrication

(K. W. R. Johnson, M. W. Shupe, C. Baker, H. Moore, R. Walker, C. W. Bjorklund)

TABLE 463-I

CARBIDE FUEL FOR REPLACEMENT PINS

	Specification	Fuel[a]
Length (in.)	0.250 ± 0.010	0.253 ± 0.004
Diameter (in.)	0.260 ± 0.002	0.260 ± 0.002
Density (% Theor.)	95 ± 2	93.1 ± 0.1
$O_2 + N_2$ (ppm)	≦ 800	609 ± 92
Metallic impurities (ppm)	low	194 ± 39
Inclusions (volume %)	< 0.5	≦ 0.02
Higher carbides	ND[b]	ND
Radiographic defects	ND	ND
Volatile gases (ppm)	low	< 1
Fuel pin pellets per pin	54	54
Archival pellets per pin	--	12

[a] Average of 4 batch preparations

[b] ND - not detectable

1. Carbide Production

The conditions necessary for routine production of carbide fuel for current EBR-II irradiation tests were developed in a series of preparations using existing equipment. Subsequent emphasis was placed on the production of carbide pellets for 4 Series 3 replacement pins. Fuel for each pin was prepared as a single batch of pellets in sufficient quantity to allow for characterization and archival specimens. Shown in Table 463-1 is a comparison of the fuel characterization with the fuel specifications. In addition to fuel for replacement pins, comparable material was produced for loading 2 archival pins. Efforts are now being directed toward production of carbide fuel for the carbide-nitride 19-pin subassembly.

2. Equipment Development

The installation of a high-temperature tungsten mesh furnace in a new recirculating inert atmosphere glove box was completed. Trial runs with stacked empty crucibles were made by heating the furnace to 2000°C in Ar, He, high vacuum and partial atmospheres of Ar.

Acquisition of the equipment for a new hydrogen treatment facility was completed and should be installed in the near future. The facility incorporates high and ultra-high vacuum components, a Pd alloy H_2 diffusion purification unit, and programmed temperature control. Furnaces and furnace tubes are interchangeable with components for a nitride synthesis facility.

A recirculating inert atmosphere glove box was transferred from another Los Alamos site to the DP Plutonium Facility. This glove box will incorporate facilities for powder processing nitride fuels. Design of this unit was completed and components for a hydride-nitride furnace were acquired.

Equipment was designed and fabricated which will increase the scale of carbothermic reductions to 120 g per preparation.

Equipment and techniques are being developed and refined for gas chromatographic analysis of the effluent gas stream from the hydrogen reduction furnaces used to adjust the carbon content of carbide fuel materials. The procedure is being used both as a process control analysis and also to provide more basic information on the carbide-H_2-CH_4 reaction. Preliminary testing has demonstrated the applicability of the chromatographic techniques for following the reaction and determining end points of the reduction; in addition, the equipment has been shown to be very useful for monitoring the nitrogen contamination levels in high purity Ar inert atmospheres.

3. Nitride Pellet Evaluation

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

TABLE 463-II

CHEMICAL ANALYSIS OF NITRIDE PELLETS

Sample No.	(concentrations in wt%)			Calculated Formula
	U	Pu	N	
8	76.5	18.23	5.36	$(U_{0.81}, Pu_{0.198}) N_{0.932}$
11	76.8	18.29	4.87	$(U_{0.81}, Pu_{0.190}) N_{0.864}$
12	76.1	18.43	5.30	$(U_{0.808} Pu_{0.192}) N_{0.943}$
13	76.1	18.41	4.58	$(U_{0.808} Pu_{0.192}) N_{0.834}$
Misc. Chunks	—	—	5.26	--

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 procedue.

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

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

TABLE 463-III

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.

The results of chemical analyses for minor contaminants are shown in Table 463-III. The O and Th concentrations are nominal, but the C content is somewhat 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-IV indicate densities that are generally between 93 and 94% of theoretical. The anamolous 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-IV

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.

4. Process Development

The basic carbothermic reduction process that is being developed for carbide production has been described previously.[1] Analysis showed the stock plutonium oxide used in the initial experiments to have a composition corresponding to $PuO_{2.53}C_{0.03}$. This was due to the presence of unconverted oxalate. A fraction of the stock oxide was reignited in air, and then used for further experiments. A mixture of uranium and plutonium dioxides and carbon was made to contain 12.18 wt% C. At equilibrium after reaction, a carbon to metal ratio of 1.1 would be expected. After a heat treatment similar to that used in earlier experiments, the reacted mass was found to be essentially single phase by metallographic examination. The chemical formula, as calculated from chemical analyses, was $(U_{0.801}Pu_{0.199})C_{0.998}O_{0.008}$. First, the U/Pu ratio remained essentially the same as the starting ratio indicating that the oxide proportions in the starting blend can be set to correspond to the desired final composition. Second, the C/M ratio in the product is slightly lower than the target, i.e., excess carbon was not present, and the oxygen concentration is slightly high as a consequence. The composition of the mixture of oxides and carbon can be adjusted to yield an increased C/M ratio sufficient to result in a product with a lower oxygen content.

A scoping test of compatibility between the reaction products and tungsten was completed. An oxide compact was reacted in close proximitry to a tungsten crucible. The carbide was found to contain an insignificant amount of W, 20 ppm, and the crucible was visually unchanged. Thermodynamic calculation predict acceptable compatibility between the CO gas and tungsten. This permits the scheduling of a tungsten mesh furnace to be used for further development of the process.

B. EBR-II Irradiation Testing

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

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

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

The fourth series is composed of nineteen singly clad fuel elements. Approximately one half of the elements will contain carbide fuel, while the remainder will contain nitride fuel. The tentative description for these experiments is shown in Table 463-VI. The test variables include fuel type, cladding cold-work, smear density, heating rate, operating temperature, and burnup. The fuel used in the fabrication of these elements will be 95% dense, single-phase $(U_{0.8}Pu_{0.2})C$ or $(U_{0.8}Pu_{0.2})N$. The carbide fuel will be fabricated from material synthesized using both arc-melting and carbothermic reduction processes. The nitride fuel for the initial loading will be supplied by Battelle Memorial Institute and will be prepared using the hydride-nitride process. The cladding tubing will be Type 316 stainless steel 0.310 in. O.D. with 0.012 in. walls. The cladding for the tests has been ordered through WADCO from Superior Tube Co. Delivery is behind schedule, but is anticipated in mid-February, 1972. The cladding will comply, as nearly as is currently available, to the fuel element cladding specification

TABLE 463-V

SERIES 1, 2, AND 3 EXPERIMENTS[a]

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

a. All elements are clad in 0.300 in. o.d. x 0.280 in. i.d. Type 316SS. All are sodium bonded elements.
b. The Series 1 and 3 experiments are fully enriched in ^{235}U. The series 2 experiments contain 97% ^{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. Capsule K-49 will be destructively examined at the request of the EBR-II Project.

TABLE 463-VI

Description of Series 4 Experiments

Element Type[a]	No. of Tests	Peak Heat Rate kW/ft	Peak Burnup a/o (MWD/MT)	Peak Cladding[b] Temperature °F (°C)	Peak Centerline[c] Temperature °F (°C)
1A	8	38.3	12.0 (105,000)	1167 (631)	1994 (1090)
1B	3	38.3	12.3 (107,400)	1157 (625)	1973 (1078)
2A	1	38.8	11.7 (102,300)	1060 (571)	1977 (1080)
3A	2	38.6	11.7 (102,600)	1167 (631)	2448 (1342)
3B	3	38.44	11.7 (102,600)	1181 (638)	2496 (1368)
4A	3	38.8	11.4 (100,000)	1078 (581)	2493 (1367)
4B	3	38.6	11.1 (97,100)	1068 (576)	2443 (1339)

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

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

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

RDT-E-13-8T. Final design of this subassembly is awaiting approval-in-principle from the AEC and design data for the new EBR-II configuration including the stainless steel reflector.

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

The status of the experiments originated by GUNFC for which responsibility has been transferred is summarized in Tables 463-VII, VIII, IX, and X. A total of 42 elements are either in EBR-II or available for insertion. Eleven elements are in the process of destructive examination. Twenty-two elements are awaiting shipment to EBR-II. The latter group will first be shipped to LASL

TABLE 463-VII

TASK 1300

EBR-II IRRADIATION EXPERIMENTS

Experiment No.	Fuel Type[a]	Fuel Density % T.D.	Clad Material	Clad Thickness, in.	Diametral Gap, in.	Fuel-to-Clad Bond	Max. Fuel Temp. at Startup, °C	Max. Linear Power, kw/ft	Current Burnup, (MWD/MT)	Subassembly Status
U93	MC + 5 v/o M_2C_3	84	316SS	0.030	0.004	He	1750	18.0	69,000	X142 - In.
U94	MC + 5 v/o M_2C_3	84	316SS	0.015	0.007	He	1680	21.9	84,000	X142 - In.
U97	MC + 5 v/o M_2C_3	84	INC-800	0.030	0.004	He	1750	18.0	69,000	X142 - In.
U98	MC + 5 v/o M_2C_3	84	INC-800	0.015	0.007	He	1680	21.9	84,000	X142 - In.
U105	MC + 5 v/o M_2C_3	84	INC-800	0.030	0.008	He	1900	16.1	58,000	X142 - In.
U106	MC + 5 v/o M_2C_3	84	INC-800	0.015	0.009	He	1825	19.8	78,000	X142 - In.
U110	MC + 10 v/o M_2C_3	99[b]	INC-800	0.015	0.014	He	1980	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	85,000	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-VIII

TASK 1960

EBR-II IRRADIATION EXPERIMENTS

Experiment No.	Fuel Type[a]	Fuel Density % T.D.	Clad Material	Clad Thickness, in.	Diametral Gap, in.	Fuel-to-Clad Bond	Max. Fuel Temp. at Startup, °C	Max. Linear Power, kw/ft	Current Burnup, (MWD/MT)	Subassembly Status
U129	MC + 5 v/o M_2C_3	84	316SS	0.022	0.016	He	1755	12.8	56,000	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	1405	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	56,000	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.

for non-destructive assay and profilometry prior to shipment to EBR-II.

A considerable effort was expended during the quarter in the routine maintenance to the fuel facility in preparation for fuel element fabrication.

C. TREAT Irradiation Testing

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

In order to assess the behavior of (U,Pu)C and (U, Pu)N fueled elements under fast reactor

TABLE 463-IX

TASKS 1930 and 1960

EBR-II IRRADIATION EXPERIMENTS

Experiment No.	Fuel Type[a]	Fuel Density % T.D.	Clad Material	Clad Thickness, in.	Diametral Gap, in.	Fuel-to-Clad Bond	Max. Fuel Temp. at Startup, °C	Max. Linear Power, kw/ft	Current Burnup, (MWD/MT)	Subassembly Status
U187	MC + 5 v/o M_2C_3	84	316SS	0.020	0.007	He	1935	30.0	45.000	Destructive Exam[c]
U189	MC + 5 v/o M_2C_3	84	INC-800	0.020	0.007	He	1935	30.0	45.000	Destructive Exam[c]
U191	MC	93	304SS	0.015	0.030	Na	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]
U205	MC + 5 v/o M_2C_3	90	316SS	0.020	0.008	He	2084	31.5	47.000	Destructive Exam[c]
U206	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 Awaiting Insertion
U190	MC + 5 v/o M_2C_3	84	INC-800	0.020	0.007	He	1935	30.0	45.000	X119A
U193	MC	93	304SS	0.015	0.030	Na	1148	31.7	47.000	X152
U196	MC + 10 v/o M_2C_3	97	304SS	0.015	0.030	Na	1132	32.6	49.000	X152
U199	MC + 10 v/o M_2C_3	97	INC-800	0.015	0.030	Na	1132	33.5	50,000	Interim
U201	MC + 5 v/o M_2C_3	84	304SS	0.015	0.008	He	2042	30.0	45.000	Interim
U207	MC + 5 v/o M_2C_3	90	316SS	0.020	0.008	He	2088	31.7	47.000	Interim
U209	MC + 10 v/o M_2C_3	97[b]	316SS	0.020	0.009	He	1909	30.9	46,000	Interim
U185	MC + 10 v/o M_2C_3	95	316SS	0.020	0.011	He	2195	30.0	< 5.000	X142 - In.
U186	MC + 10 v/o M_2C_3	95	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.
U280	MC + 10 v/o M_2C_3	98	316[d]	0.015	0.015	He	2590	34.1	——	Awaiting Shipment
U261	MC + 10 v/o M_2C_3	98	316[e]	0.015	0.015	He	2590	34.1	——	Awaiting Shipment
U262	MC + 10 v/o M_2C_3	98	INC-800	0.015	0.015	He	2590	34.1	——	Awaiting Shipment

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.

accident conditions, transient irradiations will be conducted in the TREAT facility. Investigations will be conducted on both irradiated and unirradiated fuel pins to determine (1) the threshold power levels at which damage or failure occurs, (2) the effect of bond and cladding defects, and (3) the failure propagation mechanism in multipin assemblies.

Series UL Tests

A cooperative effort has been initiated with Gulf United Nuclear Fuels Corporation in the area of TREAT testing. A series of four tests, designated LASL Series UL, will determine the effect of irradiation on the behavior of helium and sodium bonded advanced fuel elements (fabricated by Gulf United) under possible LMFBR accident conditions. Table 463-XI describes the fuel elements and test objectives. A request for approval-in-principle has been submitted to the AEC.

LASL has the responsibility for specifying the TREAT reactor test conditions and preparing the safety analysis required by TREAT for the Series UL tests. Neutronic calculations have been performed to obtain an average energy calibration factor (1.1×10^{-4} MW/cc of fuel per MW of reactor power) and its radial variation in the fuel. The edge to center power generation ratio is

TABLE 463-X

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	Awaiting shipment to LASL for pre-irradiation examination.
U242	MC	93	304SS	None	0.015	1175	35.6	Awaiting shipment to LASL for pre-irradiation examination.
U243	MC	93	304SS	None	0.030	1150	33.8	Awaiting shipment to LASL for pre-irradiation examination.
U244	MC	93	304SS	None	0.015	1175	35.8	Awaiting shipment to LASL for pre-irradiation examination.
U245	MC	93	304SS	None	0.030	1150	33.8	Awaiting shipment to LASL for pre-irradiation examination.
U246	MC	93	316SS	None	0.015	1190	36.4	Awaiting shipment to LASL for pre-irradiation examination.
U247	MC	93	316SS	None	0.030	1150	33.8	Awaiting shipment to LASL for pre-irradiation examination.
U248	MC	93	316SS	None	0.030	1140	36.4	Awaiting shipment to LASL for pre-irradiation examination.
U249	MC	93	INC-800	None	0.015	1210	36.4	Awaiting shipment to LASL for pre-irradiation examination.
U250	MC	93	INC-800	None	0.030	1145	36.4	Awaiting shipment to LASL for pre-irradiation examination.
U251	MC	93	304SS	None	0.030	1145	36.4	Awaiting shipment to LASL for pre-irradiation examination.
U252	MC	93	304SS	Vanadium-slots	0.030	1140	36.4	Awaiting shipment to LASL for pre-irradiation examination.
U253	MC	93	304SS	Iron-slots	0.030	1145	33.8	Awaiting shipment to LASL for pre-irradiation examination.
U254	MC	93	304SS	304SS-slots	0.030	1140	33.8	Awaiting shipment to LASL for pre-irradiation examination.
U255	MC	93	304SS	304SS-holes	0.030	1260	33.8	Awaiting shipment to LASL for pre-irradiation examination.
U266	MC + 10 v/o M_2C_3	98	304SS	Vanadium-slots	0.030	1140	34.0	Awaiting shipment to LASL for pre-irradiation examination.
U257	MC + 10 v/o M_2C_3	98	INC-800	Tantalum-slots	0.030	1135	33.5	Awaiting shipment to LASL for pre-irradiation examination.
U258	MC + 10 v/o M_2C_3	98	304SS	904SS-slots	0.030	1145	33.5	Awaiting shipment to LASL for pre-irradiation examination.
U259	MC + 10 v/o M_2C_3	98	INC-800	304SS-slots	0.030	1150	34.6	Awaiting shipment to LASL for pre-irradiation examination.

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

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

TABLE 463-XI

LASL SERIES UL TESTS

	TEST			
	LASL-UL-1	LASL-UL-2	LASL-UL-3	LASL-UL-4
Fuel Element[a]	163 (136 A)	164 (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	48,000	45,000
Test Objective	Fuel Melting	Fuel Melting	Same Transient as 263	Same Transient as 164

---

[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 30 - 39 kW/ft in subassembly X-055.

7.6/1. After a consideration of the capabilities of TREAT, it was decided to operate the reactor under computer control for these tests since the maximum power and total energy generated can be controlled more accurately in this mode. Heat transfer calculations, using the calculated energy calibration factor, indicate that a transient generating 70 MW for 1.4 sec, with the associated reactor startup and shut down periods, will achieve the desired results for both He and Na bonded elements. A pre-transient temperature of 260°C (500°F) was chosen. The two unirradiated elements will be tested first.

Calculations for the safety analysis required for these tests have been performed. These calculations 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. An assessment of the power generation in the end pellets of the fuel stack relative to that at the axial centerline is being made. The safety analysis is presently being written.

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 differences exist between sodium bonded, stainless steel clad, (U, Pu)C and (U, Pu)N fuels by defining failure thresholds and the types of failure experienced by these fuels. Table 463-XII summarizes the test parameters and objectives.

Two ORNL TREAT capsules[2] will be modified to incorporate a thermal neutron filter. Without the filter, an edge to center power generation ratio of approximately 10/1 would result. Calculations using rare earth metals, cadmium, boron compounds, and combinations of these materials are still being performed in an attempt to find an optimum filter.

TABLE 463-XII

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 60% 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.

A request for approval-in-principle is being prepared for this series.

III. FUEL PROPERTY MEASUREMENTS

A. Differential Thermal Analysis

(J. G. Reavis, R. Brewer)

Additional differential thermal analysis measurements have been made on irradiated UO_2-PuO_2 samples supplied by GE-Sunnyvale in a cooperative program. Samples of Pt, Rh, Ir, Al_2O_3, Pt+C, and $MoC_{0.2}$ have been prepared and used as calibration standards to reduce the uncertainty in the corrections for window absorption which must be added to the temperatures observed by optical pyrometry.

Results of the measurements are listed in Table 463-XIII. These samples were cycled several times between 1300° and selected temperatures up to and above the melting points. Good quality DTA curves were obtained for all samples up to 2100° and for samples A-1, A-2, and F3B-7 through the liquidus temperature. No arrests were observed at temperatures below the "solidus" arrests listed in Table 463-XIII, even though it is highly probable that metallic fission product inclusions were present and molten at temperatures below 2000°C. It would appear that thermal effects associated with these minor phases are below the limit of detection for the apparatus.

TABLE 463-XIII

RESULTS OF DTA OBSERVATIONS OF UO_2-PuO_2 SAMPLES IN THE HOT CELL APPARATUS

Sample No.	PuO_2, %	Burnup, atom%	Arrest Temp, °C Solidus	Arrest Temp, °C Liquidus
A-1	25	0	2790	2840
A-2	20	0	2715	2780
F3B-7	25	4.3	2745	2785
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	----

Although good quality DTA curves were obtained up to about 2100°C for samples having higher burnups than F3B-7, curves for these samples rapidly deteriorated at temperatures above 2100°C. This was caused by leakage of the sealed tungsten capsules, transport of fission products through the gas phase, and deposition of a film on the cooler portions of the furnace; including the window through which light passed to reach the pyrometer. This produced large uncertainties in temperature corrections and large irregularities in the curves. Accordingly, the last six solidus temperatures listed in Table 463-XIII should be taken as estimates with a large but undetermined uncertainty.

Additional samples of each lot of oxide remain, but additional capsule development must be done to insure against leakage and loss of samples. Since the supply of irradiated oxide is rather limited, development work will be done with other materials to the extent that this is possible.

B. High Temperature Calorimetry of Irradiated Oxides

(David G. Clifton, R. Brewer)

In an attempt to establish the accuracy of previously reported enthalpy values for irradiated and unirradiated samples of UO_2 - 20% PuO_2, a series of enthalpy measurements were made upon a sample of Standard Reference Material 720, synthetic sapphire (Al_2O_3). These values were found to be about 1 to 3% low as reported in the last quarterly report.

Efforts have been made to locate this small systematic error. A series of nine more electrical calibrations were made to confirm the energy equivalent of the calorimeter. Analysis of these calibrations resulted in an energy equivalent of 2381.3 ± .3% s.d. calories/mv.; this is about .2% higher than the older value.

New determinations were made of the correction factors to the pyrometer readings for the hot cell windows and the calorimeter sight ports. A small error was found in the older data reduction for the A factors of the sight ports. New correction curves for these were generated.

Application of these slightly altered quantities were made to the older Al_2O_3 and W data. Table 463-XIV lists these recalculated values plus three additional Al_2O_3 enthalpy determinations. The additional data were taken with a different pyrometer which has recently been calibrated by Sandia Laboratories, with a newly calibrated calorimeter sight port, and with the latest confirmed hot cell window corrections. Included in the Table are the NBS values and percentage deviation of the observed values. From these data, it is seen that the systematic error now appears to be from 0 to 2% low, excepting the one very recent point taken at 1778°C.

TABLE 463-XIV

ENTHALPY OF Al_2O_3

	$H_T - H_{25^\circ C}$, cal/gm		%
T°C	obs.	NBS	Deviation
1298	349.9	356.2	-1.8
1399	381.7	388	-1.6
1484	411.7	414.5	- .7
1583	445.9	446	0
1674	466.7	474	-1.5
1675[a]	465	474	-1.9
1778[a]	492.4	507.5	-3.0
1786	500.7	510	-1.8
1874	535	538.2	- .6
1909[a]	542.3	550	-1.4

[a] Data taken with new pyrometer.

Investigation of the possibility that a temperature gradient in the tungsten capsule may exist due to heat leaks into the support and drop mechanism was explored. A 1/2 in. O.D. x 1 3/4 in. long tungsten slug was put into a typical tungsten capsule and drops were made at 1727°C and 1781°C. The total measured energy was reduced by the amount ascribed to an empty tungsten capsule of the proper weight (as determined by the previously acquired "apparent" tungsten enthalpy curves) and the remaining energy was assigned to the tungsten slug. Assuming that radiative losses are the same for the loaded and empty capsules and furthermore assuming that if a temperature gradient exists in the system it is the same for both the filled and empty capsules, the resulting enthalpy value for the tungsten slug should be a value corresponding to some average temperature about midway in the temperature gradient. Comparison of the enthalpy value for tungsten obtained in this way with the value given in the JANAF tables gives a corresponding temperature. This temperature could be assumed to be the average temperature of the sampling. Comparison of this temperature with the observed temperature would provide some measure of the temperature gradient. Such comparisons indicated our observed temperatures to be 54° and 70°C high, respectively. Attempts to correct the Al_2O_3 data by increments of this size caused all of the Al_2O_3 data to then be about 2 to 4% higher than the NBS data.

Based on reasoning similar to the above, another series of three observations were taken at 1640, 1739, and 1810°C for a second sample of Al_2O_3 that was only about one half the weight of the previous samples. In these cases, one would expect the average temperature of the smaller charge to be closer to the observed temperature; hence, the determined enthalpy values should be closer to the NBS values. Such was not the case; in fact they were the same or slightly worse than the previous Al_2O_3 data. This possibly could be attributed to the fact that now the energy effect due to the Al_2O_3 is a smaller portion of the total measured energy and the precision of the measurements suffer.

The results of the above experiments indicate that the 0 - 2% systematic error in the Al_2O_3 enthalpy measurements is still not resolved.

It is planned to continue extending the enthalpy measurements on the irradiated and unirradiated UO_2-20% PuO_2 and concurrently to take more data on the tungsten slug and Al_2O_3 samples. The comparative feature of the irradiated and unirradiated samples of UO_2 - 20% PuO_2 should still be valid and with further information for the tungsten and Al_2O_3 samples the present accuracy difficulties should be resolved.

C. UO_2 Heat Content

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

The heat content of UO_2 has been measured by a number of different investigators in the temperature range from 483 to 3107°K.[3-8] A total of 105 data points are available in this temperature range. Each investigator normally fits his data to some functional form of temperature over the range of the data, and reports this function as a representation of the heat content. Common functions include polynomials in temperature and inverse temperature.[3,7] For use, the functions representing heat content as a function of temperature are often differentiated to obtain the specific heat. A comparison of the specific heat curves of different investigators in a temperature range where they overlap shows significant variations in the specific heat and its curvature.[7,9] This magnification of error in the slope (specific heat) of a fitted function (heat content) is well known.[10]

The object of this investigation is to fit all available heat content data for UO_2 to one function over the temperature range from 298 to 3107°K. The function must be smooth enough to provide a reasonable representation of the specific heat when differentiated. Since the heat content is normally reported as $[H(T) - H(298)]$, the function should be constrained to be zero at 298°K. The specific heat of UO_2 has been measured below 300°K by several investigators.[11,12] To make use of this information, a second constraint can be placed on the selected heat content function, i.e., fixing its slope (specific heat) at 298°K. Initially the specific heat of UO_2 at 298°K was fixed at 15.2 cal/mole °K.

Two types of functions are being investigated initially, polynomials and spline functions.[13] Polynomials have the advantage of simplicity but derivatives of fitted polynomials tend to oscillate around the true curve. Spline functions are smoother functions but more cumbersome to evaluate.[14] The spline fitting program used requires that the internal knots be specified. Thus an optimum spline function fit with a given number of internal knots cannot be obtained in a single computer run. Functions with 3 to 5 free parameters are being investigated.

IV. PUBLICATIONS

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3. M. Tokar and J.L. Green, "Hot Hardness Testing of Uranium-Plutonium Ceramics", presented at the International Symposium on The Science of Hardness Testing and Its Research Applications, Oct. 18 - 21, 1971 Detroit, Michigan.

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PROJECT 472

ANALYTICAL STANDARDS FOR FAST BREEDER REACTOR OXIDE FUEL

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

I. INTRODUCTION

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

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

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

II. ANALYTICAL CHEMISTRY PROGRAM FOR BORON CARBIDE

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

A. Status of Analytical Methods

(J. E. Rein, C. F. Metz)

In the preceding quarterly report(1), the status of analytical methods for seven chemical specifications of boron carbide pellets was reported based on a round robin sample exchange program. Improvements in the methods for the determinations of soluble boron, soluble carbon, chloride and fluoride, and metal impurities were deemed desirable on a high priority basis for use in the FFTF vendor qualification program. Improvements made in this laboratory of these methods are reported in subsequent sections. The other two laboratories, HEDL and ORNL, participating in the round robin program also improved methods. An evaluation of the improved methods is under way by means of a second round robin program. The round robin samples include a batch of pellets supplied by HEDL and special powder blends prepared at LASL.

B. Studies and Improvements of Analytical Methods

1. Emission Spectrographic Determination of Metal Impurities

(O. R. Simi, R. T. Phelps)

Boron carbide pellets and powder are analyzed for metallic impurities by a tentative emission spectrographic method described in HEDL TME-71-54, Method No. 20.4. In this method, a 20 mg portion of a mixture containing 10% B_4C sample, 22.5% GeO_2 and 67.5% graphite powder is burned to completion in a 17 amp (short circuit measurement) d.c. arc. The spectra are recorded on S.A. -1 spectrographic plates. Results are obtained by visual comparison of analytical lines in the sample spectra with spectra of calibration materials on a previously prepared calibration (reference) plate.

Several modifications of this method have been reported previously.$^{(1)}$ These are: (1) use of one set of calibration materials to contain all the required impurity elements in concentrations graded, generally, from 0.1 to 4 X the specification limits, (2) exposure of the calibration materials on the same spectrographic plate as the samples, (3) use of a grating spectrograph with a reciprocal linear dispersion of 5 Å/mm, (4) use of a centerpost electrode, and (5) addition of B_4C matrix to the calibration materials.

The major problem remaining in this method is the lack of sufficiently pure B_4C for matrix material in the calibration materials. Attempts to purify the best available B_4C by various acid leachings at atmospheric pressure were not successful. Use of a teflon-lined bomb, however, with a mixture of 3 parts HF and 1 part HNO_3 held at 150°C for 16 h reduced the impurity content of the B_4C to a level tentatively acceptable for the calibration materials. The analyses of the starting material B_4C and the purified B_4C are given in Table 472-I. Although this leaching process improved the material, it is not considered pure enough for extensive usage as matrix material.

TABLE 472-I

Purification of B_4C in a Teflon-lined Bomb

Element	Concentration of impurity element, μg/g Starting Material B_4C	Purified B_4C
Al	150	50
Bi	< 25	< 25
Ca	80	50
Co	< 50	< 50
Cr	< 100	< 100
Cu	10	< 10
Fe	700	< 200
Mg	20	< 20
Mn	< 20	< 20
Ni	< 40	< 40
Si	800	150
Ti	< 50	< 50
V	< 40	< 40
Zr	< 200	60

The list of analytical lines for visual comparison and photometric evaluation has been revised. The current lists are presented in Tables II and III. To increase the concentration range covered by several of the lines, a two-step exposure, with 100% and 15% transmission steps, is employed.

These modifications were incorporated in a method "Determination of Metal Impurities in Boron Carbide by Emission Spectroscopy" which was sent to HEDL and ORNL for evaluation. Accompanying this method were a set of calibration materials made with the purified B_4C,

TABLE 472-II

Analytical Lines for Analysis of Boron Carbide by Visual Comparison

Element	Analytical Line, Å	Concn Range, μg/g	Element	Analytical Line, Å	Concn Range, μg/g
Al	3082.2	90 to 4000	Mg	2795.5	20 to 2000
	3092.7	50 to 4000		2802.7	20 to 2000
Bi	3067.7	25 to 1000	Mn	2576.1	50 to 2000
	2898.0	500 to 1000		2801.1	50 to 2000
Ca	3968.5	50 to 450	Ni	3012.0	40 to 4000
	3179.3	450 to 4000		3002.5	40 to 4000
Co	3453.5	50 to 2000	Si	2881.6	150 to 6000
	3044.0	200 to 2000		2514.3	300 to 12,000
Cr	2835.6	200 to 4000	Ti	3088.0	50 to 2000
	2843.2	200 to 4000		3234.5	50 to 2000
Cu	3274.0	20 to 2000	V	3110.7	40 to 4000
	3247.5	20 to 2000		3118.3	40 to 4000
Fe	2599.4	200 to 20,000	Zr	3392.0	60 to 4000
	2746.5	1000 to 20,000		3438.2	100 to 4000

TABLE 472-III

Analytical Lines For Analysis of Boron Carbide
By Microphotometry

Element	Analytical Line, Å	Concn Range, µg/g	
Al	3062.2	90 to 2050	SS*
		1050 to 4050	WS*
Bi	3067.7	25 to 1000	SS
Ca	3968.5	50 to 450	WS
	3179.3	450 to 4050	SS
Co	3453.5	20 to 200	SS
	3044.0	100 to 2000	SS
Cr	2835.6	400 to 4000	SS
Cu	3274.0	20 to 500	WS
Fe	2599.4	500 to 5000	SS
		5000 to 20,000	WS
or	2746.5	2000 to 20,000	SS
Mg	2802.7	100 to 1000	WS
Mn	2576.1	100 to 1000	SS
Ni	3012.0	200 to 4000	SS
Si	2881.8	450 to 6150	WS
Ti	3088.0	100 to 2000	SS
V	3110.7	40 to 2000	SS
Zr	3392.0	50 to 2060	SS

---

* SS means strong (dark) step of the spectrum. WS means weak (light) step.

Note 1. An extrapolation of approximately $1\frac{1}{3}$ times the intensity of the highest allowed calibration blend or $\frac{3}{4}$'s of the intensity of the lowest may be used; if used, indicate extrapolation in reporting the result.

Note 2. The Ca 3179 Å line has a weak interfering line which is ignored in the calculation because it is assumed to add the same intensity to both sample and calibration blend.

a box of center-post electrodes, and a supply of GeO_2-graphite powder buffer mixture.

A longer term development effort will be made to find an alternate method for B_4C analysis. Fusion of B_4C in Na_2CO_3, with subsequent conversion of the melt to NaCl, appears to be a promising technique.

2. Determination of Soluble Boron
(R. D. Gardner, W. H. Ashley)

Work on a flame emission for measuring the soluble boron in boron carbide was discussed in the Quarterly Report for the period ending September 30, 1971 (LA-4841-MS). This work has been continued and a complete procedure has been written. A copy of the procedure has also been submitted to HEDL for comment. The samples are digested under reflux with 0.1N hydrochloric acid and with 1.6N nitric acid as described in HEDL-TME-71-54, Method 20.2, but instead of titrating the dissolved boron a small portion of the solution is purified by passage through a cation exchange column and the boron in the effluent is measured by flame emission at 5476 Å in a very lean nitrous oxide-acetylene flame.

Pellet samples were used for comparing the results by flame emission measurement with those by titration. Method 20.2, as revised by HEDL to include cation exchange purification of the extract solution before titration was used to make this comparison. Flame emission measurements of solutions of hydrochloric acid-soluble boron gave an average for 6 determinations of 0.46% with an absolute standard deviation of 0.04%. Titration of the remainders of the solutions gave an average value of 0.49% with an absolute standard deviation of 0.04%. For nitric acid soluble boron, flame emission measurements of 6 extracts gave an average value of 0.79% with an absolute standard deviation of 0.07%, and titration of the same extracts gave an average boron value of 0.73% with an absolute standard deviation of 0.07%.

The use of only a portion of the extraction solution to measure the boron proved advantageous in a study of the relationship between the amount of boron dissolved and the time of digestion. Individual samples were placed in the refluxing apparatus and the progress of the digestion was followed by withdrawing 5 milliliters of the solution at regular intervals for boron measurement. The hydrochloric acid-soluble boron seemed to be relatively constant over an acid treatment period of 1 to 5 hours, regardless of the particle size of the sample. The nitric acid soluble-boron was dependent, in some samples, on both particle size and time of digestion. A sample of powdered material showed 0.51% of nitric acid-soluble boron after 2 h, 1.91% after 18 h, and 2.62% after 25 h. Some crystalline material was crushed and sieved into two fractions

(100-200 mesh and -200 mesh). The hydrochloric acid-soluble material was removed before applying the nitric acid digestion. Under these conditions the coarser fraction showed no significant increase of dissolved boron after the first hour of acid treatment analyzing 0.31% after 1 h and 0.34% after 7 h of treatment. The finer portion yielded 0.55% after 1 h and increased regularly to 0.79% after 7 h of treatment.

A sample of pelletized material was ground and sieved in the same way. The hydrochloric acid-soluble part was not separated in advance. The nitric acid-soluble boron was constant in both size fractions, yielding 0.8% at the end of 2, 3, and 4 h respectively. Another portion of the same material was followed for 112 h and increased only to 1.1% during that time.

Nothing was found in this study to suggest any better way to dissolve the free boron than the digestion conditions proposed in HEDL-TME-71-54. For its measurement, however, flame emission technique seems to have advantages.

3. Determination of Soluble Carbon

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

The cause of high bias in the soluble-carbon values has been found and corrected. The fault lay in not drying the effluent stream of nitrogen sufficiently before measuring the carbon dioxide. The manometric apparatus described in the HEDL tentative procedure (Method 20.1) has been constructed and its performance verified by the collection and measurement of known amounts of carbon dioxide derived from a sodium carbonate standard solution. Using this apparatus, further analyses have been made on a mixture of pellets. Eight soluble-carbon values on this material gave an average value of 0.50% with a relative standard deviation of 12%. The reported HEDL average value was 0.69% and the relative standard deviation was 9%. The two clusters of values actually touch. This agreement is probably sufficient for any present purpose.

On another series of pellet samples method 20.2 from HEDL-TME-71-54 was used except that a HEDL modification involved a temperature change from 100°C to 100-110°C for the acid digestion step. The performance of the apparatus was checked during the analysis of this series by measurement of carbon dioxide from a sodium carbonate standard solution. During the acid-digestion period a thermometer was immersed in the oxidizing reagent and kept at a reading of 105 ± 2°C. A total of 7 determinations were made with an average of 1.15% and a relative standard deviation of 7%.

It was found that the measured soluble carbon is not very sensitive to the duration of the acid-digestion treatment. The analyses of pellets described above gave an average for 8 determinations of 0.50% after a digestion time of 1 h. When 4 additional portions of this material were treated for 1.5 h, the soluble carbon was found to increase only slightly to 0.52%. On the other hand, increasing the digestion temperature from 100 to 110°C resulted in an increase from 0.50 to 0.67% for the soluble carbon value, in 12 determinations. When the scatter of individual measurements is considered, this effect is not great. Further increase to 120°C for 3 determinations confirmed the trend, giving an average measured value of 1.17%.

Further Dissolution Studies With Sulfuric Acid-Dichromate Reagent

Work has been done also on the dissolution rates of boron and carbon in the sulfuric-sodium dichromate reagent. A spectrophotometric method using methylene blue[(2)] was used for measuring the dissolved boron. The method depends upon the formation of BF_4^- by treatment with dilute HF solution, reaction of the complex ion with methylene blue, and extraction of the colored product with dichloroethylene. The applicability of the method to the analysis of the digestion solution was verified with known amounts of boric acid added to the reagent solution. The sensitivity of the method is great enough so that only 100 microliters of the digesting solution is required for an analysis, and the result is accurate to a few percent. In the operation of the soluble carbon apparatus the nitrogen sweep gas is interrupted and the apparatus retains any carbon dioxide evolved during the measurement time. It is possible to analyze a single sample by measuring successive increments of carbon dioxide at any chosen time interval, and the 100-microliter sample for boron determination may be taken at the same time.

Ground samples were analyzed in 1 h intervals, using a 100-milligram sample and a digestion temperature of 100°C. In these materials the rates of dissolution of boron and carbon were greatest during the first hour diminishing to a constant rate in 4 or 5 h. Succeeding intervals, up to 10 h in some cases, showed no further change. Figure 472-I is a typical plot showing the trend of the values. The atom ratios of boron and carbon that dissolved after 5 h corresponded to the formula B_4C, and there was no apparent change in the rate of dissolution per hour that might be attributed to depletion of the reagent. The soluble-carbon was calculated from the measurements of carbon dioxide made after an hour of leaching was found to be 0.93 and 1.00% in two analyses that were followed by digestion treatments of 8 and 6 h. The value was confirmed by three more determinations which were terminated at 1 h with soluble-carbon values of 0.93, 1.00, and 0.87%.

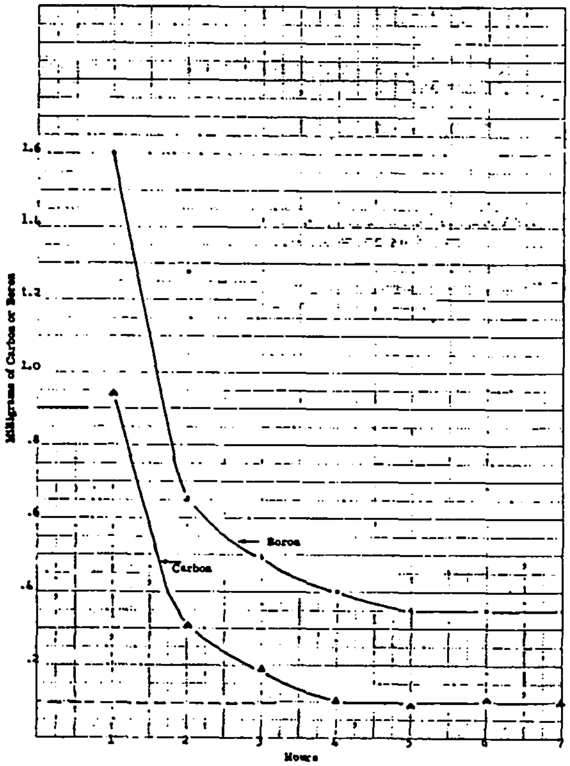

Fig. 472-I Rate of Dissolution of Powdered Samples Expressed as Mg Per Hour

The fine material, which passed a 200-mesh sieve, was also analyzed. The first experiment was terminated with loss of the sample after obtaining the measurement of soluble carbon following 1 h of leaching -- 1.27%. In the second experiment the leaching was allowed to continue for 6 h and gave a value for the soluble carbon of 1.17%. The soluble carbon in this material was therefore approximately 20% greater than that in the 100-200 mesh fraction when both were measured according to the HEDL procedure. Other observations on the analysis of the finely ground material were understandable on the basis of particle size. The absolute amounts of both boron and carbon dissolved in 1 h were 2 or 3 times as great, but there was little change in the shape of the plot of weight rate of dissolution versus time.

Inspection of Fig. 472-I suggests that the soluble carbon measured after 1 h should be corrected by subtracting an estimate of the boron carbide dissolved during that hour. The assumption that the boron carbide dissolution is constant from the start (the dotted line in Fig. 472-I) is a tempting one, and this approach has been used by Kitahara(3). It has also been stated(4) that the rate of attack on B_4C is lower during the early part of the digestion when most of the free carbon is dissolved. Evidence on this point was sought as follows: Digestion with 1.6M nitric acid removed boric acid, soluble boron, and possibly some free carbon as well, producing the nearest thing to pure boron carbide available at present. Some nitric acid digested material from a previously treated material from which the -200 mesh fraction had not been removed, was washed, dried, and analyzed. In these experiments, the carbon and boron were measured at 10-min intervals during the first hour and hourly thereafter. The absolute amounts of boron and carbon to be measured were small, so the sample size was increased to 150 milligrams and the boron determinations were made on duplicate 100-microliter portions. The plot of boron and carbon values looks very much like Fig. 472-I, except that the rapid initial dissolution rate declined very sharply to a constant rate by the end of 1 h. The ratio of the weights of boron and carbon was quite constant during the first hour at 2.7 (B_4C would be 3.6), indicating that the soluble carbon was not removed by the nitric acid pretreatment but was dissolved during the first hour of oxidation. There appears to be no indication of slower initial dissolution of B_4C.

A correction to the measured soluble carbon value, based on the constant rate of dissolution of B_4C observed after 3 to 5 h digestion, does not appear justified. The experiments with nitric acid-extracted material indicate that boron carbide dissolution is more rapid in the first hour, so the simple extrapolation shown by the dotted line in Fig. 472-I would not be correct, and the time required to reach the horizontal part of the curve would be largely wasted. As the HEDL recommended procedure stands, it ignores two biases of opposite sign. There is a positive bias introduced by the solubility of B_4C and a negative bias from ignoring the carbon dioxide produced after the first hour. Since a legitimate correction for the solubility of B_4C is lacking, it is probably best to let both biases stand until additional work proves otherwise.

III. ANALYTICAL CHEMISTRY PROGRAM FOR LMFBR/FFTF FUEL

A. Calibration Materials and Quality Control Samples

(J. E. Rein, R. K. Zeigler, R. T. Phelps, C. F. Metz)

The powder blends of metal and nonmetal impurities in matrices of uranium-plutonium mixed oxide, uranium oxide, and plutonium oxide, prepared for use as calibration materials and quality control samples have been sent to HEDL for the fuel pin vendor qualification program. The transmittal letter to the HEDL Quality Assurance Section included recommended limits for the analytical results on the quality control samples.

B. Determination of O/M Atom Ratios

(J. W. Dahlby)

The determination of O/M atom ratios in mixed oxide fuels was investigated further by comparing results obtained at LASL and HEDL using two thermogravimetric methods on one lot of sintered $(U,Pu)O_2$ pellets. In the method used at LASL, the pellets were dried in helium at 120°C, weighed, oxidized in air at 1000°C, and then reduced at 1000°C in helium containing 6 at.% hydrogen. At HEDL, the weighed pellets were heated to 800°C in argon containing 8 at.% hydrogen and water vapor at a partial pressure of 4 mm. In each case, the change in weight was used in calculating the O/M atom ratio. To eliminate possible bias caused by heterogeneity or different storage or handling conditions, personnel at HEDL ramdomly chose forty pellets from a batch which had been previously analyzed and determined to be homogeneous in O/M ratio. Twenty of the pellets were shipped to LASL while the remaining 20 pellets were stored in an identical shipping container at HEDL. Each of the shipping containers was opened on the same day and the measurements of O/M ratios were started immediately by each laboratory.

The average of 1.964 ± 0.002 obtained at LASL for the O/M ratio on eight samples each containing 3 grams of crushed $(U,Pu)O_2$ sintered pellets compared well with the average of 1.961 ± 0.004 obtained at HEDL. It was concluded that either method gave the correct result for O/M ratio on sintered $(U,Pu)O_2$ pellets.

C. Development of Fuel Burnup Measurement Methods

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

A sequential separation method has been developed(5) that gives separate fractions containing plutonium, uranium, and neodymium for subsequent mass spectrometric measurements. This method, designed for burnup analysis on mixed uranium-plutonium fuels, involves only two separation operations. A portion of the dissolved fuel with added isotope spikes of ^{150}Nd, ^{233}U, and ^{242}Pu is fumed with perchloric acid and transferred in $12\underline{M}$ hydrochloric acid to a 10X anion exchange resin column. The effluent containing neodymium, higher transuranics, and most other fission products is fumed with nitric acid and transferred in a mixture of $0.8\underline{M}$ HNO_3-90% methanol chromatographically separates the higher transuranics and rare earth fission products to give a clean neodymium fraction. Plutonium is eluted from the 10X anion exchange resin column with a $12\underline{M}$ hydrochloric acid - 0.1M hydroiodic acid mixture followed by uranium with 0.1M hydrochloric acid.

This method has been used successfully for a wide variety of experimentally irradiated FBR fuels in the 401 Program. The neodymium chromatographic separation takes about 4 h and is done in custom-fabricated glass columns. Modifications are being evaluated to increase the speed of separation and to use "throw away" inexpensive plastic columns. These modifications consist of changes in the nitric acid strength and water-methanol composition of the loading and eluting solutions. The use of stronger nitric acid and lower methanol content is promising.

IV. PAPERS PRESENTED AT MEETINGS

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

2. "Survey of Analytical Methods in the Nuclear Fuel Cycle", by C. F. Metz and G. R. Waterbury. Presented at the "Symposium on the Analytical Chemistry of the Nuclear Fuel Cycle", sponsored by IAEA in Vienna, November 28-December 2, 1971.

3. "The Determination of Non-Metallic Specification Impurities in Mixed-Oxide Reactor Fuel", by C. F. Metz and G. R. Waterbury. Presented at the "Symposium on the Analytical Chemistry of the Nuclear Fuel Cycle", sponsored by IAEA in Vienna, November 28-December 2, 1971.

4. "Status of Burnup Measurement Methodology", by J. E. Rein. Presented at the "Symposium on the Analytical Chemistry of the Nuclear Fuel Cycle", sponsored by IAEA in Vienna, November 28-December 2, 1971.

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

6. "Preparation and Characterization of Reference Material for the Chemical Specification Analysis of Uranium-Plutonium Mixed Oxide Fuel and Source Materials", by J. E. Rein, R. T. Phelps, W. H. Ashley, G. R. Waterbury, C. F. Metz. Presented at the "Symposium on the Analytical Chemistry of the Nuclear Fuel Cycle", sponsored by IAEA in Vienna, November 28-December 2, 1971.

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

8. "Analysis of Advanced Reactor Fuels", by G. R. Waterbury and C. F. Metz. Presented by G. R. Waterbury at the 162nd National Meeting, American Chemical Society, Washington, D. C. September 12-17, 1971.

V. REFERENCES

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5. "Quarterly Status Report on the Advanced Plutonium Fuels Program, April 1 to June 30, 1971, and Fifth Annual Report, FY 1971", LA-4749-MS, Los Alamos Scientific Laboratory (1971), p. 57.

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