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EXAMINATION OF FAST REACTOR FUELS, FBR ANALYTICAL
QUALITY ASSURANCE STANDARDS AND METHODS, AND
ANALYTICAL METHODS DEVELOPMENT—Irradiation Tests

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Compiled by

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ABSTRACT

This is the eighth quarterly and second annual report on the Examination of Fast Reactor Fuels and FBR Analytical Quality Assurance Standards and Methods at the Los Alamos Scientific Laboratory. Since the first quarterly report (LA-5798-PR), the Analytical Quality Assurance Standards and Methods project has been divided into the following two projects.

FBR Analytical Quality Assurance Standards and Methods

Analytical Methods Development-Irradiation Tests

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

PROJECT AL 001

EXAMINATION OF FAST REACTOR FUELS

Person in Charge: R. D. Baker
Principal Investigators: W. T. Wood
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 Reference Fuels System Branch of DRDD. 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 DRDD.

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 microexaminations 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 and other chemical analyses.

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. In-Cell Equipment

(F. S. Abeyta, G. R. Brewer, A. L. Bridge, W. R. Carter, F. J. Fitzgibbon, M. E. Lazarus, J. M. Ledbetter, H. Martinez, P. A. Mason, F. H. Newbury, A. G. Nicol, J. A. Romero, T. J. Romero, D. S. Shaffer, L. N. Vikdal, J. J. Villareal)

1. The cell where heat content measurements were made was converted to a fuel pin and capsule sectioning cell during the year. The heat content apparatus and related hardware were removed from the alpha box and stored for possible future requirements. All new electrical power and instrumentation conductors and a variety of liquid and gas supply lines were installed. A recirculating O₂ and H₂O purifier was installed along with inert atmosphere purge and pressure differential control systems.

New equipment installed in the box includes a sectioning saw and jig assembly. The jig incorporates a pin positioning trolley capable of being placed into position in 25.4-mm (1.000-in.) increments of length and it has a 25.4-mm (1.000-in.) travel slide with dial micrometer. Positioning of fuel pins and capsules for transverse sectioning is possible to accuracies of ± 0.05 mm (± 0.002 in). The vacuum cleaner assembly contains an integral blower and HEPA filter with a standard one-gallon can serving as the dust collector. The can is easily sealed with a standard lid and transferred through the 17.8-cm (7-in.)

transfer port into a disposable 17.8-cm (7-in.) plastic alpha can. The vacuum is attached to a high velocity duct configuration of the saw assembly during sectioning operations and also serves for general cleanup requirements in the alpha box. This will reduce cleanup requirements and radiation exposure levels of personnel during cell equipment maintenance or modifications. Alpha tube transfer ports for both the standard O-ring sealed alpha transfer tubes and Swagelok cap seal transfer tubes were installed.

This alpha box has been in operation since September 1975.

2. The former arc spark spectrometer alpha box was modified for installation of the General Electric oxygen potential meter apparatus. Since the box was originally intended to be operated with an air atmosphere and an inert gas atmosphere is required for the operation of the oxygen potential meter, extensive modifications were required to seal the box adequately and install inert atmosphere purge and pressure differential control systems. The electrical, gas, and liquid services were also revised.

The alpha box has been installed in a hot cell and is presently undergoing final equipment check-out. The oxygen potential meter is expected to be placed in the cell next quarter so that it can be evaluated under remote conditions.

3. The Data Acquisition-Computer System for the Wing 9 optical profilometer, which will be used on breached elements, is under construction and is approximately 80% complete. This includes the computer system and associated electronic equipment. Quotations for the design and fabrication of the electro-optical sensor have been received and are being reviewed. The Wing 9 profilometer system is similar to the DP-West system with the following exceptions:

a. It will have capability of FORTRAN programming and magnetic disk loading of programs.

b. It will have an x-y plotter for immediate confirmation of acceptable profilometry data.

c. It will have sufficient memory to apply bow angle error corrections to the data and it is recorded on magnetic tape.

4. The Data Acquisition-Computer System for the DP-West optical profilometer is now operational. This system greatly simplifies data acquisition and operates 2.5 times faster than the old system.

The Automatic Centering System for the DP-West optical profilometer is also operational. Those elements with bows up to 25 mm (1 in.), which could not be "profiled" before, are now being measured.

5. A shutter system for shielding an interim storage hot cell window from excessive radiation was designed and installed. The shield consists of two 50-mm (2-in.) lead shutters placed on a ramp which is set at an angle from horizontal sufficient to allow the shutters to close under their own weight. Each shutter is opened by a manually operated winch.

6. The initial pressure drop in the DP-West fission gas sampling system when puncturing pins or capsules with a high fission gas content was found to be caused by electrical conduction across the sensing electrodes in the Baratron head. According to MKS Baratron, this has been found to occur when radioactive gases (Kr, Xe) are present at a pressure > 0.14 atm absolute in the dual electrode type heads. These heads have measuring electrodes on both the reference and pressure sides of the diaphragm. The problem was eliminated in FY 1976 when a new Baratron head with a measuring electrode on the reference side only was received, calibrated, and placed in service.

7. Fabrication of parts for the new Laser Drilling/Welding System for fission gas sampling has been completed. Installation and testing in the cell will start next quarter. The advantage of this system over the existing design is the ability to reweld fission gas sampling holes for future element storage or possible reinsertion in a reactor.

8. Fabrication of a new inert atmosphere disassembly alpha box and high acid chemical analysis alpha box continued during FY 1976 see Fig. AL 001-1. The disassembly box is essentially complete. It incorporates a new, improved mechanical profilometer design with an accuracy of ± 0.005 mm (± 0.0002 in.), pulsed eddy current device, fission gas sampling system, high pressure leak test system, 10X and 30X periscope for viewing fuel pin and

Fig. AL 001-1. Alpha boxes for the disassembly and chemical analysis cells.

capsule cladding, Kollmorgen Model 301 periscope, macrophotography stand, fuel pin storage magazine, and a 17.8-cm (7-in.), 45.7-cm (18-in.), alpha tube, and sphincter transfer systems. Provisions have also been made for the future installation of an optical profilometer.

Special features of the disassembly box include the elimination of many elastomer seals, use of double-seal design for the large viewing window with annulus pressurized with inert gas, remotely replaceable periscope viewing windows, and quick-removal assemblies of the inert gas purge and pressure differential control panels. The 17.8-cm (7-in.) and 45.7-cm (18-in.) transfer systems include "fail as is" interlocks in the electro-pneumatic control systems to prevent exposing the box to air in the event of a power outage.

Installation of the disassembly box has been delayed by the completion and check-out of several electronic components. These are now 95% complete. The final equipment and box leak tests are presently in progress with installation in the hot cell scheduled to begin during the next quarter.

The replacement high acid chemical analysis alpha box will incorporate a manually operated air lock transfer system, a 17.8-cm (7-in.) can transfer port, a 12.7-cm (5-in.) drop tube port, an analytical balance located above the hot cell shielding with cable supported tray, a centrifuge installed in a floor well, a magnetic

stirrer, a hot plate, a sealed tube dissolution furnace, a pH meter, and numerous stainless steel supply lines for a diversity of gas and liquid supply requirements. An acid fume hood and scrubber assembly will also be installed in addition to a drain connected to the Wing 9 Facility high acid level drainage system. The box will be installed after the disassembly box is in operation.

Three new-design collimator plugs, see Fig. AL-001-2, were fabricated during the year with port dimensions of 15.240 mm (0.600 in.) by 19.050 mm (0.750 in.), 3.175 mm (0.125 in.), and 6.350 mm (0.250 in.). The plugs were fabricated by machining an outer brass cladding with end caps and port mandrels. The assemblies were cast with a low background radiation grade lead in an induction furnace. After cooling, the mandrels were removed by a tensile test machine. X rays performed at the Betatron Facility verified the void free casts. An aluminum liner was also machined and installed in the collimators lead shielding block. The purpose of the brass

Fig. AL 001-2. New collimator plug.

cladding and aluminum liner were to eliminate galling and distortion of the collimators as had occurred with the original all-lead units.

10. A special tool, see Fig. AL001-3, for deencapsulating damaged fuel elements was designed and fabricated. This tool permits accurate circumferential cutting and removal of the capsule without damage to the encapsulated fuel pin. The cutting speed and rotation are remotely controlled by a console located outside the cell. The capsule can also be rotated manually if it is extremely out of round.

11. A fission gas sampling system was constructed and is operational at the Wing 9 facility. It is used as a backup system for the DP-West unit and also provides an increased fission gas sampling capability.

12. Additional capacity for storing irradiated fuel elements was provided with the installation of a cart system below an operating table in one of the hot cells. The cart is remotely operated and moves into the corridor for loading and unloading. It can physically accommodate 500 fuel elements (100 in each of 5 "Rover Inserts" containing a neutron absorber). The actual limit on the number stored, however, may be limited by the radiation level in the cell. The operating table will contain a 10-cm (4-in.)-thick lead shield.

13. An ion etcher gun assembly, procured and modified by personnel from the microstructural analysis section, was adapted for remote operation in the metallograph blister. Auxiliary equipment, including the vacuum

system, was installed and tested. Remote operation to determine the optimum parameters for etching irradiated fuel specimens was completed and the etcher is now being applied routinely to fuel specimens.

14. A special welding fixture for the automatic welding of residual fuel storage capsule end caps in an inert atmosphere has been designed. The fixture is capable of being mated to any of the inert atmosphere cells via "45.7-cm (18-in.) transfer port." The fixture is capable of sealing stainless steel capsules of 12.7-mm (1/2-in.) to 19.0-mm (3/4-in.) o.d. by 0.89-mm (0.035-in.) wall thickness. Tubing lengths up to 1.55 m (61 in.) can be handled. The sealed capsules will provide inert storage for residual fuel sections and reencapsulation of fuel components for off-site shipment. Fabrication is expected to begin next quarter.

15. A replacement macrophotography sample holder with black anodized surface was fabricated for the metallography section. The black surface is expected to improve the quality of the metallography sample macrographs by reducing reflected light.

16. An order has been placed with Programmed and Remote Systems (PaR) for a Model 300C bridge-mounted manipulator to replace one of the hot cell corridors' General Mills Model 300 manipulators presently in use. The replacement was necessitated due to the deteriorated condition of the manipulator and unavailability of replacement parts. Delivery is scheduled near the end of the 1976 calendar year.

17. New fuel pin storage tubes incorporating Swagelok end caps for a primary seal are being fabricated. The tubes have been approved for off-site shipments of radioactive materials and are inexpensive to fabricate. Two remotely operated fixtures were designed and fabricated for inerting the tubes. One of the units will be installed at the Wing 9 Facility and the other at the DP-West Facility.

18. Six inert atmosphere storage cans which mate with the 17.8-cm (7-in.) transfer ports were fabricated during the year for storage of mounted metallography specimens. These cans incorporate a ball-check pressure relief valve and particulate filter in the can lid assembly to prevent over pressurizing the cans due to possible outgassing of mounted specimens during long term storage.

Fig. AL 001-3. Precision saw for cutting cladding.

19. A revision to the design of the 45.7-cm (18-in.) transfer can has been completed which incorporates a flexible joint at the lid and port adapter ring. The change allows a relaxation of the alignment requirements to remotely mate and seal the can to the alpha box 45.7-cm (18-in.) ports.

20. A 100-mm (4-in.)-thick tantalum collimator block with a 7.874-mm (0.310-in.) bore was fabricated for special gamma scanning requirements to determine the radial power profile associated with the examination of the HC1 TREAT experiment for the Argonne National Laboratory (ANL). Tungsten rods ranging in diameter from 0.762 mm (0.030 in.) to 6.350 mm (0.250 in.) and 100 mm (4 in.) in length were fabricated with two thin plastic disks of 7.849-mm (0.309-in.) outer diameter cemented near each rod end.

21. A crate has been designed for the disposal of the disassembly and sectioning cell alpha box. Various schemes are being devised to permit the remote decontamination of the alpha box interior to a low radiation level to permit removal of the box from the cell, insertion into its crate, and transport to the radioactive materials disposal site.

22. Two hundred and thirty metallographic grinding gages were fabricated for the mounting of specimens during the year. These gages incorporated steps and sloping surfaces accurate to ± 0.025 mm (± 0.001 in.) to provide visual verification that the metallographic longitudinal specimens have been ground to their major diameters.

Approximately 500 metallographic sample potting fixtures were fabricated for the mounting of specimens during the year. These fixtures consist of 31.750-mm (1.250-in.)-inside diameter aluminum sleeves of equal length and 6.350-mm (0.250-in.)-thick Teflon disk machined to a light press fit in the sleeves to serve as a bottom seal. After the potting resin has hardened, the mount is pressed from the fixtures with a pneumatic press.

23. Two replacement waste compactor assemblies and autoradiograph press adapters were fabricated during the report period. One of these units was installed in the metallography cells.

24. Shields of 50-mm (2-in.)-thick lead were designed for attachment to the interchange box located in the decontamination room to reduce the radiation exposure of personnel. Fabrication is scheduled for the next quarter.

B. Development Work and Maintenance of Manipulators (A. L. Bridge, W. R. Carter, J. M. Ledbetter, P. A. Mason, E. L. Mills)

1. Twenty-one master-slave manipulators required overhaul or major repair work during the year.

2. The booting of 26 master-slave manipulator arms required replacement during the year.

3. The telescoping tube hoist cable required replacement on a General Mills Model 302 manipulator. A defective bridge travel limit switch was also replaced on a General Mills manipulator.

4. The wrist adapter assembly and the grip and wrist rotation drive motors of a General Mills Model 302 manipulator were accidentally crushed by a hot cell shielding door. Parts from a spare manipulator were used for replacement.

5. Two surplus General Mills Model 302 manipulators and controls were recently obtained from the Nevada Test Site. These manipulators are in excellent condition and will extend the useful life of manipulators of this type installed at the Wing 9 and DP-West facilities. The surplus spare parts for the manipulator were also obtained from the site.

6. Several different fabrication techniques were attempted during the year to extend the life of inflatable inner tubes used to form a seal between the master-slave manipulator through tubes and the alpha box ports. Viton and hypalon coating were applied to reduce dry-rotting effects. These coatings extended the life of the tubes from approximately two months to four months, but the lack of resistance to radiation and heat of the tubes' butyl rubber compound prevented extending the useful life significantly.

A special wiper seal, similar in configuration to an oil seal, has been designed for insertion into the standard Central Research Laboratory (CRL) manipulator booting

seal collar as a possible replacement for the inflatable inner tubes. Two of these seals have been molded and installed on manipulators located at the fuel pin and capsule sectioning cell for evaluation.

III. ANALYTICAL CHEMISTRY

A. Gamma Scanning

(B. K. Barnes, A. S. Murray, J. R. Netuschil,
J. N. Quintana, J. R. Phillips, T. K. Marshall)

A new PDP-11/40 central processing unit was installed as the computer-based terminal to process the gamma scanning data. A computer code was developed to generate 1-to-1 axial plots of the gross gamma and isotopic distributions. These 1-to-1 plots allowed the principal investigator to compare readily the gamma scanning results with the engineering drawings and other 1-to-1 plots of profilometry and eddy current data. The code was modified to allow long 1-to-1 plots (greater than 1050 mm) to be plotted automatically during the night. The data were entered during the daytime, stored on magnetic tape or on magnetic disk, retrieved, and plotted under program control without the presence of an operator. This modification eased the daytime load on the computer-based terminal and allowed more efficient utilization of the limited computing resources.

The principal data processing code, SURVEY, was modified to detect automatically all the statistically significant full-energy gamma-ray peaks, with these energy regions being staged to LASL's Photostore storage device for permanent storage. This new option eliminated two manual processing steps of the data and reduced the total data processing time by one day. The use of Photostore made possible unlimited archival storage, thereby eliminating the use of magnetic tapes as the principal storage technique.

In addition to the previous modification reducing the physical volume of the archive data, the program was converted to provide microfiche copies of the printed computer output. This option reduced the volume of stored gamma scanning records by several orders of magnitude. The implementation of the two new options significantly reduced the volume of records and has provided the capability of long term storage of raw and processed data.

The processed gamma scanning data have been transmitted to the experimenter on magnetic tape as well as on 1-to-1 plots and computer listings. A program was written to generate these magnetic tapes locally using the computer-based terminal, thereby improving turnaround and eliminating the transporting of the tapes to and from the central computing facility. The program used the same external BCD code and format as the CDC-7600 system, so the data format was transparent to the requester.

Several minor modifications were performed on the data acquisition system. A computer program was written and implemented on the PDP-8/L computer of the scanning unit to calculate the proper rotation and tilt of the fuel pins for correct alignment after a single set of measurements. This method of alignment proved to be considerably faster than the previous multiple measurement method.

The method for energy stability of the data acquisition was improved by eliminating the use of pulser as reference lines for the gain stabilization system. An IAEA ^{22}Na gamma-ray source was used for reference lines. As the ^{22}Na gamma-rays are subject to the same conditions as the gamma rays from the fuel pin, the gain shifts in the spectra were considerably reduced.

The possibility was investigated of using gamma scanning as a method for determining retained fission gas. The 514-keV gamma ray of ^{85}Kr was the principal gamma ray investigated, but the nearby 512-keV gamma ray of ^{106}Rh appeared to completely obscure the ^{85}Kr line. A mixed-carbide and a mixed-oxide fuel sample were scanned without significant results. The examination of older fuel samples (the ^{106}Ru - ^{106}Rh isotope has a 369 d half-life) has been initiated.

The backup gamma scanning system, including a ND-160 pulse height analyzer, magnetic tape unit, Ge(Li) detector and shield, was used to scan a low-activity fuel pin following its irradiation as TREAT. The extremely low activity of this fuel pin required scanning outside of a hot cell. Prior to the destructive sectioning of the test capsule, both axial gross gamma and isotopic scans were obtained. After sectioning, three pellets were scanned diametrically to measure the radial power profile. The individual pellets were mounted in a specially designed

holder and scanned using a set of 1.5^o conical gold tantalum collimators. We have designed a new tantalum-tungsten collimator assembly which should improve the precision of the gamma scan data obtained from similar low-activity test capsules. The new design is presently being evaluated using known geometric sources.

B. Ultrasonic Microsamples

(J. W. Dahlby, A. P. Lovell)

As a possible alternative to using the gamma scanning system for measurement of the radial power profiles of TREAT capsules, the use of an ultrasonic impact grinder for obtaining samples to be analyzed by radiochemistry was evaluated. An ultrasonic impact grinder was set up and tested in a glove box for obtaining microsamples from cross sections of ceramic reactor fuel pellets. A slurry of abrasive grit in Dowanol was the grinding medium for an ultrasonically tuned, stainless steel, grinding needle. Core samples having 0.64-mm diameters and weighing up to 10 mg were obtained from a UC pellet. A dial indicator, registering to 0.025 mm, was used to estimate the sample location measured from the pellet edge. This instrument and microcoring technique worked best on unfractured pellets.

C. Determination of Oxygen Potential in Irradiated Oxide Fuels

(D. Temer, A. Lovell, J. Dahlby)

The solid-state electrochemical oxygen potential meter obtained from General Electric was evaluated and modified for remote hot cell operation. The following modifications and/or improvements were made:

1. A brake switch was added to the sample table motor to permit the operator to stop exactly at preselected points on the pellet. Without the brake, calibration and pellet measurements were extremely difficult and time-consuming.

2. A temperature controller was installed on the furnace to precisely maintain the specified temperature ($\pm 1^{\circ}\text{C}$) at which the oxygen potential measurements were recorded.

3. A microswitch was added to the control apparatus to prevent the sample table rotation motor from activating accidentally. This safety feature will prevent the accidental turning of the sample table when it is in contact

with the probes, thereby reducing the possibility of breakage.

4. To permit convenient remote control manipulator operations, a junction box housing the wires from the two probes, the sample table, and the two thermocouples was mounted at the side of the head plate of the instrument. This arrangement removed the wires to a more convenient location.

5. Precision metering valves with electric solenoid switches were installed to control the speed of raising and lowering the sample table and also the unit from the furnace.

6. The Tygon pneumatic supply lines were replaced with stainless steel lines.

7. Standards duplicating the Cu/CuO, Fe/FeO, and Ni/NiO materials supplied by GE have also been fabricated at LASL.

Two major problems were encountered during evaluation of the instrument. The first problem involved the binding of the sample table shaft in the guide tube. The first few times this occurred, the instrument was disassembled and the shaft and collar areas of the guide tube were sanded and polished. This action temporarily eliminated the binding, but the problem recurred. Later, it was discovered that the upper and lower collar areas of the guide tube for the central shaft were not properly aligned, and heating and cooling caused the lower collar areas of the shaft to warp. Both the upper and lower collar areas were reamed in an attempt to solve this frustrating problem. If this corrective action is not successful, periodic complete disassembly of the instrument remotely will be required to repair the instrument after it is installed in a hot cell.

The second problem was failure of the platinum wire that provided electrical contact from the top of the probe to connectors outside of the probe guide. The probe, when in contact with a pellet, was pushed up slightly and then returned to its original position when the pellet was removed. This up and down movement broke the platinum wire after a short time. A complete dismantling of the apparatus was necessary to repair the broken wire. An easy solution to this design problem was not found.

The instrument is presently being installed in a shielded hot cell where it will be evaluated under remote conditions.

D. Determination of Carbon in Uranium or Plutonium Carbide Materials

(V. Dahlby, H. Kavanaugh, A. Lovell)

The method for gravimetrically determining carbon in irradiated materials was improved by using I_2O_5 - SiO_2 reagent in place of CuO to oxidize CO to CO_2 . This oxidizing reagent was convenient for hot cell use because it oxidizes CO efficiently at room temperature. Repeated determinations of carbon in SRM 276 (NBS tungsten carbide with a certified carbon content of 6.09%) made under remote conditions averaged 6.10% carbon with a standard deviation of 0.01₅ and a relative standard deviation of 0.25%. This method also was applicable to trace carbon analysis in irradiated materials by applying a manometric measurement of the CO_2 . An efficient method for making 500-g batches of the oxidizing reagent was developed.

E. Determination of Burnup

(S. F. Marsh, M. R. Ortle, J. A. Alarid,
C. F. Hammond, R. M. Abernathy, J. E. Rein)

The increasing throughput of samples for this analysis has depleted the supply of the triple (^{233}U , ^{242}Pu , ^{150}Nd) spikes used in the ^{148}Nd mass spectrometric method for measuring burnup. A new series of almost 1060 spikes was prepared and then calibrated using two standardizing materials for each of the three spike components. Although only the relative concentrations of ^{233}U , ^{242}Pu , and ^{150}Nd were required for the burnup measurement, the spikes were prepared as weighed aliquots having known absolute ^{233}U , ^{242}Pu , and ^{150}Nd atom contents in each tube. These data provided a capability to determine the absolute uranium, plutonium, and neodymium isotope contents of samples when using sample aliquots delivered on a weight (or volume) basis.

F. Measurement of Retained Fission Gases by Isotope Dilution Mass Spectrometry

(R. M. Abernathy)

An isotopic spike-mass spectrometric determination of fission product gas retained in irradiated reactor fuels was developed and put into semiroutine use. The internal standard was a mixture in argon of krypton and xenon, enriched in their light isotopes, that was prepared manometrically and verified by mass spectrometry. A

precisely known amount of the internal standard mixture was added to the fission product gases as they were released during dissolution. The final mixture of gases was collected by cold-trapping and analyzed by mass spectrometry. Addition of the internal standard eliminated the need for quantitative collection of the gases and permitted correction for any uncollected fraction. Quality Assurance procedures describing this method were written and approved.

G. Computer Modification of Thermal Ionization Mass Spectrometer

(R. M. Abernathy, J. K. Wooten, E-5)

A 1.2-million word magnetic disk and hardware-extended arithmetic element have been added to the data acquisition system on the AVCO mass spectrometer. This enabled the use of more efficient FORTRAN programming, easier program modification, and storage of specialized programs for uranium, plutonium, and neodymium measurements for burnup analyses. The special programs contain peak locations and mass differences for discrimination corrections which formerly required operator input through the teletype. Calculation of atom percent burnup was revised to provide better accuracy.

H. Shielded Electron Microprobe

(W. F. Zelezny, J. D. Farr, J. M. Hansel)

The shielded electron microprobe was used to investigate possible axial migration of burnup monitor Nd in mixed uranium-plutonium carbide fuels. In only one mixed carbide-sesquicarbide fuel, having undergone 7.8 at. % burnup, was any evidence found for axial migration of neodymium and associated fission products. A deposit of fission products on the top metallic (tungsten) insulator plug in this sample was determined to contain plutonium and significant concentrations of neodymium, cerium, praseodymium, palladium, and rhodium, very little ruthenium, and no uranium. Ruthenium occurred in appreciably higher concentrations in the nearby fuel material.

These inconclusive results of rare earth fission product migration observed by microprobe examination and some past evidence from gamma scanning data of the axial migration of cerium in mixed oxide fuels indicate that this investigation should be continued in greater detail.

I. Quality Assurance Computerization

(J. H. Dahlby, A. P. Lovell, J. R. Phillips)

The quality assurance computer programs were modified to provide a listing of the current index of all analytical chemistry Quality Assurance procedure numbers and titles as required by the QA program.

The computerized index resulted in significant time savings in updating the storage file and in obtaining complete index listings for the entire group or for any of the eight specific sections. All of the required QA information could be instantly accessed from any of the six time-sharing terminals in the group.

A detailed description of the computerized record keeping programs was prepared for publication as a Los Alamos Scientific Laboratory report.

IV. MICROSTRUCTURAL ANALYSIS

(K. A. Johnson, E. C. Walter)

The technician cross-training program has continued this year in all the microstructural areas.

Cut or roll film with automatic processing has been applied to the photocopy area. Cut film has also been applied to the "selected area" type photomicrographs. Strips and mosaics are the only areas of irradiated fuel pin microscopy not as yet using cut or roll film.

In FY 1976, 307 samples were processed. This, after accounting for a 15% manpower reduction, is a 28% increase in productivity over FY 1975, or 3.5% counting only samples.

Work has been started on the installation of a digital height gage for use in remote sequential grinding of samples in the grinding cell.

A complete review has been initiated on the QA data record system to improve both its quality and particularly efficiency by reducing redundancy.

QA certified ASTM-based microhardness of irradiated samples can now be routinely done, but it does interfere directly with remote optical microscopy.

The remote Leitz metallograph was overhauled this year and major cell repairs were required after seven years of use. (The microstructural alpha cells went gamma hot in September of 1969.) This combined maintenance operation accounted for three-fourths of the

approximate four weeks of cell downtime for this fiscal year.

The Mark Six model ion etcher was installed for the remote operations etching of irradiated fuel/clad samples. The unit is now being applied routinely to both carbide and oxide fuels. Samples having over 12% burnup have been very satisfactorily etched in addition to many at lower burnup levels.

V. REQUESTS FROM DRDD

Examination of Irradiated Materials

(R. M. Abernathey, K. A. Johnson, M. E. Lazarus, R. A. Morris, J. R. Phillips, E. C. Walter, G. R. Waterbury, W. T. Wood, W. F. Zelezny)

During FY 1976 the fuel elements (oxide and advanced) received for examination in each of the four quarters are shown in Table AL 001-I.

General Electric Company: Twenty-two irradiated fuel pins were received in FY 1976. Examinations performed on 68 irradiated fuel pins are listed in Table AL 001-II.

During 1974, 218 archive samples of unirradiated mixed-oxide material were received and stored. This year 123 samples were sent to recovery and 95 samples remain in storage.

Hanford Engineering Development Laboratory: Fifty-eight irradiated fuel pins were received in FY 1976. Examinations performed on 136 irradiated fuel pins are listed in Table AL 001-III.

TABLE AL 001-I

IRRADIATED FUEL ELEMENTS RECEIVED IN FY 1976

<u>Fiscal Year</u> <u>Quarter</u>	<u>Advanced</u> <u>Fuel Type</u>	<u>Oxide</u> <u>Fuel Type</u>
1st	--	6
2nd	11	18
3rd	1	84
4th	--	25
Total	12	133

TABLE AL 001-II

POSTIRRADIATION EXAMINATIONS OF CAPSULES
AND PINS FROM GE

Examination	No. of Capsules or Pins Examined
1. Visual Examination	25
2. Preliminary Measurements	25
3. Profilometry, Optical	26
4. Radiography	24
5. Gamma Scan, Gross	26
6. Gamma Scan, Multispectral	17
7. Gas Sampling and Analysis	20
8. Photography, Full Length	25
9. Photography, Incremental	10
10. Sodium Removal	4
11. Wire Wrap Removal	16
12. Eddy Current	25
13. Sectioning, Pin	13
14. Sectioning, Cladding	4
15. Density Measurements	13(59) ^a , [15] ^b
16. Microprobe Analysis	4
17. Burnup Analysis	17 (52) ^a
18. Scribe Reference Marks	28
19. Diameter Measurements, Micrometer	1
20. Clad Removal	1
21. Density Preparation, Cladding	18(41) ^a , [15] ^b
22. Optical Microscopy ^c	17(62) ^a
23. EMX Preparation and Photography	9 (10) ^a

^aNumbers in parentheses in this and following tables refer to number of samples.

^bNumbers in brackets refer to unirradiated fuel pins in this and following tables.

^cThe optical microscopy includes macrophotography, alpha autoradiography, beta-gamma autoradiography, and as-polished and etched photomicroscopy, (including mosaics) in inert (N₂) atmosphere. Specimens from other experimenters' fuel pins were examined in like manner.

TABLE AL 001-III

POSTIRRADIATION EXAMINATIONS OF CAPSULES
AND PINS FROM HEDL

Examination	No. of Capsules or Pins Examined
1. Visual Examination	57
2. Preliminary Measurements	66
3. Profilometry, Optical	67
4. Radiography	55
5. Gamma Scan, Gross	17
6. Gamma Scan, Multispectral	54
7. Gamma Scan, Fuel Column Length	9
8. Gas Sampling Analysis	19
9. Photography, Full Length	69
10. Photography, Incremental	20
11. Wire Wrap Removal	54
12. Eddy Current	36
13. Sectioning	22
14. Density Measurements	3 (18)
15. Microprobe Analysis	12
16. Burnup Analysis	23 (37)
17. Retained Fission Gas Analysis	6 (16)
18. Scribe Reference Marks	1
19. ¹³⁷ Cs, Pu, U Analysis	1
20. U, Pu Analysis	4 (5)
21. ¹³⁷ Cs Analysis	5 (6)
22. Two-Dimension Scan	4
23. Optical Microscopy	14 (93)
24. EMX Preparation and Photography	18 (23)

Irradiated fuel pins P-23C-B3, P-23C-B5, and 23 sections taken from irradiated fuel pins HEDL-P-15-1A, P-15-14A, P-15-25B, P-15-38B, and P-15-49C were shipped to Hanford Engineering Development Laboratory (HEDL) at Richland, Washington on April 15, 1976.

Temperature monitors removed from irradiated fuel pins HEDL-P-15-55C, P-15-38B, P-15-12A, P-15-83D, and P-15-93D, were shipped to HEDL at Richland, Washington on June 1, 1976.

Twenty-seven sections removed from irradiated fuel pins HEDL-P-59-62, P-20-5, P-20-8, P-20-28, and P-20-36 were shipped to HEDL at Richland, Washington on June 10, 1976.

Los Alamos Scientific Laboratory: In this section, examinations of carbide and nitride fuel elements are discussed. The technical evaluation of these elements is being conducted by LASL personnel under the Advanced Fuels Program.

Eleven irradiated fuel pins were received during FY 1976. Examinations performed on 55 fuel pins are listed in Table AL 001-IV.

Westinghouse Advanced Reactor Division: Forty-eight irradiated fuel pins were received during FY 1976. Examinations conducted on 48 fuel pins are listed in Table AL 001-V.

Argonne National Laboratory: Examinations conducted on the one irradiated fuel element (ANL-HCl-TREAT experiment) received in FY 1976 are listed in Table AL 001-VI.

VI. SUPPORTING WORK

A. Filter Changers

(F. J. Fitzgibbon, D. S. Shaffer, W. A. Stone)

A replacement mechanism for raising and lowering the absolute filters in the Wing 9 hot cell filter chambers was designed and installed last year. Sixteen mechanisms were installed in the cell filter chambers and 12 in the decontamination room filter changer.

The original system did not allow for surface irregularities in the absolute filter chambers. Masonite shims of various thicknesses were used to get the filters to seal properly and the operation was very time consuming.

The new design (fabricated of aluminum and brass) is simple, inexpensive, and readily adjusts to variations in the absolute filter chambers giving a uniform pressure to the filter gasket and making an extremely reliable seal. Downtime required to change the filters was also reduced with the new design.

TABLE AL 001-IV
POSTIRRADIATION EXAMINATIONS OF CAPSULES
AND PINS FROM LASL

Examination	No. of Capsules or Pins Examined
1. Visual Examination	39
2. Preliminary Measurements	38
3. Profilometry, Optical	163 (91)
4. Profilometry, Mechanical	7
5. Radiography	17
6. Gamma Scan, Gross	13
7. Gamma Scan, Multispectral	3
8. Gas Sampling and Analysis	38
9. Photography, Full Length	40
10. Photography, Incremental	40
11. Photography, Kollmorgen	2
12. Eddy Current	13
13. Sectioning	17
14. Density Measurements	17 (66)
15. Microprobe Analysis	10 (11)
16. Burnup Analysis	18
17. Diameter Measurements, Micrometer	2
18. Pressure Leak Tests	3
19. Bonding Removal	21
20. Clad Removal	21
21. Split Pin Cladding	2
22. NaK Removal	2
23. Dissolution for SEM	1
24. SEM Sectioning	2 (3)
25. Wire Wrap Removal	2
26. Optical Microscopy	17 (63)
27. EMX Preparation and Photography	13 (18)
28. SEM of Irradiated Cladding	5 (5)
29. Sequential Grinds	1 (20)

B. Cell Window Maintenance

(F. J. Fitzgibbon, G. R. Herrera, J. M. Ledbetter, R. J. Reynolds, J. J. Villareal)

A procedure, used by Oak Ridge National Laboratory, to remove deposits from the interior surfaces of lead glass windows was used successfully to clean two hot cell window assemblies at Wing 9. The window cleaning was

TABLE AL 001-V
POSTIRRADIATION EXAMINATIONS
OF PINS FROM WARD

Examination	Pins Examined
1. Visual Examination	48
2. Preliminary Measurements	47
3. Profilometry, Optical	13
4. Radiography	37
5. Gamma Scan, Gross	19
6. Gamma Scan, Multispectral	14
7. Photography, Full Length	2
8. Photography, Incremental	2
9. Eddy Current	48
10. Pin Weight	38
11. Pin Length Measurement	21

TABLE AL 001-VI
POSTIRRADIATION EXAMINATIONS OF CAPSULE
AND PIN FROM ANL

Examination	No. of Capsules or Pins Examined
1. Visual Examination	2
2. Preliminary Measurements	2
3. Profilometry, Optical	1
4. Radiography	2
5. Gross Gamma Scan	1
6. Multispectral Scan	1
7. Radial Gamma Scan	3
8. ¹⁴⁰ Ba Activity	3
9. Gas Sampling and Analysis	1
10. Photography, Incremental	1
11. Eddy Current	1
12. Bonding Removal	1
13. Sectioning	1
14. Clad Removal	1
15. Optical Microscopy	1 (5)

performed by a filling and draining technique while the windows remained in place. The windows were restored nearly to the original state of clarity as judged by visual observation.

Following the draining of the mineral oil a 1:1 mixture of toluene and isopropyl alcohol was used to rinse the oil from the glass surfaces. Glacial acetic acid then removed the deposit from the glass and rinses with toluene-isopropyl alcohol removed the acetic acid. This procedure required five days for each window assembly.

C. Shipping Casks

(F. J. Fitzgibbon, P. A. Mason, W. T. Wood)

Construction of the new radiography cask continued during this quarter. Completion of the cask, which is being constructed under Quality Assurance Procedures, has been delayed and is now expected during September 1976. Approval will then be obtained for off-site shipments of radioactive materials.

Modifications to the last 2 (10 total) "Rover Casks" completed during the second quarter were inspected, prior to painting, at HEDL by a Los Alamos Scientific Laboratory representative to ascertain compliance of the casks as intended with the proposed alterations. The modifications were accepted by a LASL representative and this brings the casks into compliance with ERDA requirements.

LASL representatives attended a meeting during the first quarter of FY 1976 at Idaho National Engineering Laboratory relative to the shipping of potentially contaminated materials from Hot Fuel Examination Facility-North (HFEF-N). It was hoped that some design or procedural change would be implemented by ANL-W to permit the continued use of shipping casks such as the LASL-5885 and HEDL RM-29 containers. These casks would be a significant asset in the future for the transportation of fuel columns from Fast Flux Test Facility (FFTF) pins and other fuel elements up to 100 mm (40 in.) in length.

Additionally, it was hoped that ANL-W would give serious consideration to developing a system whereby shipments made to LASL would be free of contamination. An ANL-W representative visited LASL during the last quarter to review the problems associated with receiving contaminated shipments.

D. Accountability of Fissile Material

(K. E. Dowler, F. J. Fitzgibbon)

An itemized inventory of all fuel pins, fuel pin sections, and other accountable fissile material was performed and the data were transferred to an existing computer program administered by the LASL Nuclear Materials Group. Some portions of the computer program, which were not applicable to accountability for the CMB-14 Group, were used to tabulate and show location of nonaccountable items such as metallography specimens and fuel pin hardware.

E. CHIT Program

(K. E. Dowler, J. R. Phillips)

A review of and revisions to the "CHIT" cost accounting program were completed. Since its inception approximately two years ago, considerable time and effort has been spent in refining the program to its present state. Since this general type of cost accounting could be adapted to other fuel pin examination facilities, a report entitled "CHIT: A Cost Accounting Program for Postirradiation Examinations of Fast Breeder Reactor Materials" (LA-6114) was prepared and issued in November 1975. Since the completion of this report, a few additions have been made to the program that now make the summary output acceptable as a quarterly throughput report.

F. Other Requests

(K. E. Dowler, F. J. Fitzgibbon, K. A. Johnson)

The 93 irradiated fuel pins received in FY 1975 from HFEF-S were made ready for hardware removal for eventual shipment to the Savannah River Laboratory (SRL) for storage and eventual recovery. All the required pre- and postirradiation data have been received and assembled. Information related to the packaging safety and criticality analysis has been approved. Eight pins from the group were returned to HEDL for further examination at their facility. The remaining pins are being held awaiting approval from HEDL for sectioning and shipment to SRL.

Assistance was provided CMB-8 in shipping of activated Al disks to the University of Cincinnati. Assistance was also provided CMB-5 in the shipping of 40 mg of radioactive ^{235}U , ^{238}U , ^{237}Np and ^{239}Pu to the Argonne National Laboratory in Argonne, Illinois.

Eight SEM samples of irradiated cladding were prepared and examined for ANL-W.

VII. QUALITY ASSURANCE

(L. E. Lanham)

Analytical Chemistry

1. A training session was held for members of CMB-1 to discuss Quality Assurance documentation. New employees were given a QA indoctrination lecture.

2. Thirty-three analytical procedures have been reviewed and approved by QA.

3. The documentation was reviewed and the shipping container inspected by surveillance personnel for two shipments.

Hot Cell Operations

1. An audit was conducted by CMB-QA on April 22, 1976. All operations were audited for compliance to RDT Standard F2-2. An audit report has been written and approved by program management. Action has been initiated on all findings of this audit.

2. Two procedures for hot cell examinations have been reviewed and approved by QA.

3. The shipping procedures and inspection documentation has been reviewed for three shipments.

Microstructural Analysis

Two QA procedural documents were reviewed.

Nondestructive Testing

Four QA procedural documents were reviewed.

VIII. PUBLICATIONS

1. John R. Phillips, "Improved Nondestructive Determination of Two-Dimensional Radial Isotopic Distributions in Irradiated Fuel Pin," *Nuclear Technology* **28**, 282-290 (February 1976).
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3. J. R. Phillips, T. K. Marshall, G. R. Waterbury, "Differences in the ^{103}Ru and ^{106}Ru Axial Distributions in (U,Pu) O_2 Fuel Pins," submitted for publication to the *J. Inorg. Nucl. Chem.*
4. J. W. Dahlby, J. R. Phillips, "The LASL Computerized Quality Assurance Record Keeping System for Analytical Chemistry," Los Alamos Scientific Laboratory report in preparation.

PROJECT AL 003

FBR ANALYTICAL QUALITY ASSURANCE STANDARDS AND METHODS

RESEARCH AND DEVELOPMENT

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

I. INTRODUCTION

Reliable chemical characterizations are essential to the development of high-quality fuels, control rods, and other reactor components in the FBR program. The objective tasks are designed to assure the quality of the chemical characterizations necessary to evaluate reactor components relative to specifications. Tasks include: (1) the continual preparation and distribution of carefully characterized calibration materials and quality control samples for use in quality assurance surveillance programs of vendor and purchaser analytical chemistry laboratory operations, (2) the development of and the guidance in the use of quality assurance programs for sampling and analysis, (3) the development of improved methods of analysis, and (4) the preparation of continuously updated analytical method manuals. At this time, the emphasis is on the FFTF. The program will be extended, as appropriate, to the LMFBR demonstration and large production facilities in the future.

II. ANALYTICAL CHEMISTRY PROGRAM FOR MIXED OXIDE FUEL

A. Reference and Quality Control Materials

(F. R. Roensch, J. V. Pena, J. E. Rein)

As a major continuing task, calibration and quality control materials were prepared and distributed to FFTF fuel vendors, Atlantic Richfield Hanford Company (ARHCO) as supplier of the plutonium source material, and Hanford Engineering Development Laboratory (HEDL) as reactor operator. New series of calibration blends of nonmetal impurities in matrices of $(U, Pu)O_2$ and PuO_2

were prepared. Overcheck analyses verified makeup values except for the erratic, high fluoride levels in the PuO_2 matrix blends. The supply of calibration and quality control materials for both metal and nonmetal impurities in PuO_2 matrix was nearly exhausted. The HEDL continued attempts to obtain PuO_2 batches with suitably low levels of impurities to be used for preparing new series of blends.

The batch of 1000 $(U, Pu)O_2$ pellets that had been packaged in the first quarter of FY 1976 for use as quality control samples for the O/M determination proved unsatisfactory. Based on a joint HEDL-LASL investigation, the O/M drifted upward nonuniformly from an initial value of < 1.97 to > 1.99 while in storage under vacuum before LASL packaging. Apparently, there were either some oxygen (air) or moisture traces in the storage container.

In the last quarter, a batch of about 1000 $(U, Pu)O_2$ pellets with an O/M value < 1.94 and packaged in a dry helium atmosphere was received from HEDL. Our analysis of 10 pellets agreed with HEDL's value to indicate that stability was maintained. This batch of pellets is being packaged with a single pellet in each glass ampoule that is sealed in an electric furnace (hot wire) in a glove box installation in which the atmosphere is dry argon.

A paper, prepared jointly with HEDL, was presented at the IAEA "International Seminar on Nuclear Fuel Quality Assurance."¹ This paper presented all aspects of the QA program in operation since 1972 for the chemical

analysis of the mixed oxide fuel manufactured for the FFTF. Topics covered were (1) fuel and source material chemical specifications, (2) requirements and tests for laboratory qualification, (3) preparation, characterization, packaging, and record keeping of calibration and quality control materials, (4) administration of the program including the tabulation and charting of quality control results, and (5) operational experiences.

A computer program was prepared to calculate the decreasing plutonium content and changing plutonium isotopic composition of plutonium calibration and quality control materials as a function of time. The decay of the five plutonium isotopes (238, 239, 240, 241, and 242) is considered, and the monthly output is the changed data.²

B. Determination of Sulfur (D. J. Temer)

A recently obtained (Dohrmann-Envirotech) sulfur analyzer is being evaluated for determining sulfur in U-Pu fuels. The sample, in a resistance-heated tube furnace, is reacted with flowing oxygen to produce SO_2 which is continuously titrated with internally generated iodine in a null-balance microcoulometer cell.

An evaluation by the manufacturer using LASL-prepared calibration materials in uranium oxide matrix and preliminary experiments with the instrument at LASL are encouraging, both from the accuracy and speed-of-analysis standpoints.

III. ANALYTICAL CHEMISTRY PROGRAM FOR LOW-FRICTION, HARD SURFACES (J. E. Rein, R. K. Zeigler, G. R. Waterbury)

The objective of this HEDL-LASL cooperative effort is to provide an analytical chemistry program for the chemical characterization of chromium carbide hard surfaces to be applied as a molten blend to various structural components of the FFTF reactor. The analytical methods, a manual containing these methods, a QA plan covering the production operation, and most of the needed reference materials except high-purity Cr_3C_2 are on hand. A source of pure Cr_3C_2 has not yet been found. A proposed round robin evaluation of analytical capabilities still awaits transfer from HEDL to LASL of Cr_3C_2 powder, nichrome powder, and hard surface product.

IV. ANALYTICAL CHEMISTRY PROGRAM FOR METALLIC CORE COMPONENTS (W. H. Ashley, E. A. Hakkila, M. E. Smith, J. E. Rein, G. R. Waterbury)

The draft of the HEDL-LASL prepared RDT Standard FI-3 "Analytical Chemistry Methods for Metallic Core Components," was approved for issue by RDD without significant changes. This document contains chemical, x-ray fluorescence, and emission spectrographic methods for the determination of major and minor elements in various stainless steels and inconels.

V. ANALYTICAL CHEMISTRY PROGRAM FOR BORON CARBIDE (W. H. Ashley, R. D. Gardner, A. L. Henicksman, F. R. Roensch, J. E. Rein, G. R. Waterbury)

The HEDL reported that the QA program associated with the production of boron carbide pellets as the FFTF control rod absorber material continued satisfactorily for all chemical specification measurements. The previously supplied calibration materials and quality control samples provided reliable analytical chemistry operations at the vendor and HEDL laboratories, and minimum between-laboratory differences. A previous difficulty reported for the empirical soluble carbon determination³ has not reappeared.

VI. REFERENCE ANALYSES (J. W. Dahlby, C. H. Ward)

During the year, randomly selected pellets of two (U, Pu) O_2 productions lots were analyzed for O/M ratio. Results were provided to HEDL to aid in establishing the cause for a small, consistent difference in O/M measurement between a vendor and HEDL.

VII. REFERENCES

1. J. E. Rein, R. K. Zeigler, G. R. Waterbury, W. E. McClung, P. R. Praetorius, and W. L. Delvin, "Quality Assurance Program for Surveillance of Fast Reactor Mixed Oxide Fuel Analytical Chemistry," IAEA International Seminar on Nuclear Fuel Quality Assurance, Oslo, Norway, May 24-28, 1976.
2. S. F. Marsh, W. D. Spall, R. M. Abernathy, and J. E. Rein, "Correcting Plutonium Calibration Materials for Assay and Isotopic Changes," Los Alamos Scientific Laboratory report, in preparation.

3. R. D. Baker, *Quarterly Report, "Examination of Fast Reactor Fuels, FBR Analytical Quality Assurance Standards and Methods, and Analytical Methods Development-Irradiation Tests, October 1 - December 31, 1975,"* Los Alamos Scientific Laboratory report LA-6229-PR (February, 1976).
2. J. E. Rein, R. K. Zeigler, G. R. Waterbury, W. E. McClung, P. R. Praetorius, and W. L. Delvin, "Quality Assurance Program for Surveillance of Fast Reactor Mixed Oxide Fuel Analytical Chemistry," IAEA International Seminar on Nuclear Fuel Quality Assurance, Oslo, Norway, May 24-28, 1976.

VIII. PUBLICATIONS

1. RDT F11-3, "Analytical Chemistry Methods for Metallic Core Components," U.S. ERDA Report, approved for publication. Prepared jointly by HEDL and LASL.
3. S. F. Marsh, W.D. Spall, R. M. Abernathy, and J. E. Rein, "Correcting Plutonium Calibration Materials for Assay and Isotopic Changes," Los Alamos Scientific Laboratory report, in preparation.

PROJECT AL 014

ANALYTICAL METHODS DEVELOPMENT - IRRADIATION TESTS

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

I. INTRODUCTION

Necessary to the development of high-quality fuels and other reactor components required by the FBR program are highly reliable analytical methods for the measurement of burnup, oxygen-to-metal (O/M) ratio, and various gases in irradiated fuels.

The tasks of this program include: (1) the development and proof testing of burnup methods based on chemical separation-thermal ionization mass spectrometry, on analyses using inexpensive apparatus, and on spark source mass spectrometry for rapid, precise measurements; (2) the development of methods for the measurement of oxygen-to-heavy metal atom ratio (O/M) of unirradiated and irradiated fuels, and the establishment of conditions for the preparation of reference materials; and (3) the development of methods for the measurement of gases and their release rates as functions of temperature and time.

II. DETERMINATION OF BURNUP

A. Determination of Low Burnups of Mixed Uranium-Plutonium Fuels

(S. F. Marsh, M. R. Ortiz, R. M. Abernathey, J. E. Rein)

Low burnups (0.001 to 0.5%) of mixed uranium-plutonium fuel are determined by a recently developed method¹ in which three ion exchange resin columns are used to separate fractions of neodymium, uranium, and plutonium for isotope dilution mass spectrometric measurement. Following dissolution of the sample, uranium and plutonium are retained on the first column of anion exchange resin from strong HCl. The fission products and

uranium pass through the column, and only the rare earth group is then retained on a second column of pellicular cation exchange resin from HCl-CH₃OH.² Neodymium subsequently is isolated from the rare earth group by chromatographic elution from a third anion exchange resin column using a HNO₃-CH₃OH medium. Plutonium is eluted from the first column with a HI-HCl mixture followed by the elution of uranium with dilute HCl.³

Two portions of the dissolved fuel, one without dilution for the neodymium measurement and the other weight diluted for the uranium and plutonium measurements, are added to separate weighed portions of a ¹⁵⁰Nd-²³³U-²⁴²Pu triple spike blend. This technique conserves costly ²³³U and ²⁴²Pu spike materials and uses the same triple spike blends prepared for higher burnup fuels.

B. Chemical Techniques Using Inexpensive Apparatus

(S. F. Marsh, M. R. Ortiz, J. E. Rein)

Burnup measurement methods are being developed and evaluated to complement the technique of chemical separation-isotope dilution mass spectrometry either for applications that do not warrant the high precision ($\leq 0.5\%$ relative standard deviation) or for use in laboratories that do not have mass spectrometers. The first chemical procedure developed using low-cost apparatus incorporates ion exchange resin separation of uranium, plutonium, and total rare earth fission products (as the fission monitor) followed by spectrophotometric determination of each.^{4,5}

The second technique being investigated is a micro-complexometric titration of uranium, plutonium, and total rare earth fission products (as the fission monitor) using ion selective electrodes as the end point sensors. Titration

of a rare earth mixture (in proportions simulating FBR fission products) uses ethylenediaminetetraacetic acid (EDTA) as the titrant, equimolar Cu-EDTA as the indicator, and a copper-selective electrode as the end point sensor. The titrant reacts with the rare earths and the completion of this reaction is signaled by a slight excess of EDTA that shifts the Cu-EDTA equilibrium as detected by the copper-selective electrode. This system has been used to measure 56 nmol of simulated fission-proportion rare earths with a relative standard deviation of 1%.

The initial system being investigated for the measurement of uranium involves a reduction of uranium to U^{4+} , which forms stronger complexes than U^{6+} with EDTA and similar complexants, and then a titration using a cadmium-selective electrode as the end point sensor. This electrode is used rather than a copper-selective electrode because reducing agents for U^{6+} reduce Cu^{2+} to Cu^{1+} , which is not complexed by EDTA and similar complexants. The initial reductant investigated was sodium formaldehyde sulfoxylate⁶ which does not introduce metal ions. Initial success was obtained, but results subsequently became erratic, perhaps because of a reaction of the electrode with sulfur-containing reaction products from the sodium formaldehyde sulfoxylate. Metal reductants, such as magnesium and thallium, were tried without success. Other reductants evaluated with no or limited success included sodium sulfite (Na_2SO_3), sodium dithionite ($Na_2S_2O_4$), sodium dithionate ($Na_2S_2O_6$), formamidine sulfonic acid [$H_2NC(NH)SO(OH)$], formaldehyde ($HCHO$), hydrazine (N_2H_4), and hypophosphorous acid (H_3PO_2). Electrolytic reduction of U^{6+} to U^{4+} , which does not introduce reagents that can interfere with the ion selective electrode measurement, currently is being investigated with a variety of media and electrodes, using solid-electrode polarography to evaluate each system.

A titration to an ion selective electrode end point likewise is planned for plutonium, preferably as the Pu^{3+} ion. Any reductant system that produces U^{4+} also should reduce plutonium to Pu^{3+} . It seems likely, therefore, that uranium and plutonium would be determined together in a single titration. This is desirable, not only because of the time saved, but also because the prior chemical separation could be simplified.

A third chemical burnup technique that is to be investigated is liquid chromatography. Advantages of this technique are (1) high sensitivity, which should allow use of smaller samples that reduce exposure of personnel to ionizing radiation; (2) enhanced separation capability, commonly providing multicomponent separations within an hour; and (3) measurement of separated sample constituents on the same instrument. Most of the materials and equipment needed for the liquid chromatography study have been received.

C. Spark Source Mass Spectrometry

(R. M. Abernathy, W. D. Spall, J. E. Rein)

A program is under way to develop burnup procedures using the recently installed spark source mass spectrometer which provides wide-range isotopic measurement of all elements with high and roughly comparable sensitivities. A major objective is to incorporate the multispike isotope dilution technique with a minimum of chemical operations to determine accurately and rapidly relative amounts of fission product, uranium, and plutonium isotopes. From these determinations, total fissions (or burnup) can be computed. A later goal is to measure simultaneously several fission products to compute relative fissions produced by the various fissionable uranium and plutonium isotopes.

The capability of the instrument for the burnup determination is being established using both photoplate and electrical detection. From data collected during the specification performance tests, the measured relative standard deviation for the $^{148}Nd/^{150}Nd$ ratio of natural neodymium using the electrical detection system was 7%. The major factor limiting the precision was a relatively high signal-to-noise ratio of the system. Electronics instrumentation specialists are evaluating modifications to improve performance. Precision of photoplate measurement has been evaluated using a synthetic 1% burnup fuel in solution having a weight ratio of 1/1000 neodymium/uranium. In this evaluation, sample mounting techniques of solution evaporated on graphite electrodes and of solution evaporated on silver powder and pressed into electrodes were used. The sample analyzed contained 1 mg uranium and 1 μ g neodymium with no preceding chemical treatment. This quantity as irradiated fuel would have

a radiation level, essentially at contact, of about 50 mR/h which would require minimum shielding for personnel safety. The precision of the neodymium and uranium isotope abundance values generally were < 5% relative standard deviation using a densitometer for line intensity measurements. On this basis, the predicted precision of the overall burnup measurement is better than 7%. Spark excitation times were ≤ 5 sec for uranium and about 12 min for neodymium taken sequentially on the same sample. Including between-sample pumpdown time, an analysis rate of one sample/h appears attainable.

III. DETERMINATION OF O/M RATIO IN SOLID SOLUTION (U, PuO_2) (G. C. Swanson, G. R. Waterbury)

The crystal defect structure of solid solution uranium-plutonium oxide FBR fuels affects many fuel operating parameters. The O/M ratio is a measure of the fuel defect structure; hence its accurate determination is important. The major objective of this task is to prepare reference materials of high accuracy for this determination.

Previously, data were presented for the correlation of oxygen potential and the O/M ratio for UO_2 and PuO_2 ⁷ prepared by oxidizing the pure metals under carefully controlled conditions. A solid solution ($\text{U}_{0.775}\text{Pu}_{0.225}\text{O}_2$) reference material was then prepared by alloying weighed quantities of pure uranium and plutonium metals in an yttrium oxide crucible, and oxidizing the alloy with moist helium at 250°C. The oxygen potential-O/M relationship was measured for this material over the temperature range of 800°C to 1300°C (Fig. AL 014-1). The oxygen potential change for ($\text{U}_{0.775}\text{Pu}_{0.225}\text{O}_2$) is considerably larger at O/M = 2.000 than is calculated from the data obtained for $\text{UO}_{2.000}$ and $\text{PuO}_{2.000}$.

Use of a reference oxygen potential of -100 kcal/mol produced an O/M ratio of 2.000. However, the equilibrium time required to produce the 2.000 ratio is excessively long. For this reason, the use of physical standards prepared from high-purity metals is recommended for calibration purposes.⁸

The high-temperature oxygen electrode described last year⁷ produced a stable, but nontheoretical EMF.

Fig. AL 014-1. Oxygen potential of ($\text{U}_{0.775}\text{Pu}_{0.225}$) oxide from 800°C to 1300°C.

IV. DEVELOPMENT OF GAS MEASUREMENT TECHNIQUES (W. D. Spall, R. M. Abernathy, J. E. Rehn)

The initial apparatus designed for measurement of gases released from materials under programmed heating cycles of temperature and time has been completed and its capabilities determined. Major components are an inductively heated vacuum furnace, a gas-transfer pumping system, a series of gas-collection bulbs, a Baratron pressure-measuring system, and a Varian MAT CH-5 gas mass spectrometer. A Datatrac programmer provides constant temperature or reproducible temperature-time cycles. The available temperature range is 400 to 1900°C for graphite crucibles and 400 to 2600°C for tungsten crucibles. The maximum temperature rise rate, limited by induction heater response for the present configuration, is 250°C/min. Temperature reproducibility

and stability decrease significantly at rates greater than $100^{\circ}\text{C}/\text{min}$, becoming greater than 10% relative. The lowest usable rate, limited by long term stability in the heater power supply, is $50^{\circ}\text{C}/12\text{ h}$. Isothermal temperature reproducibility after settling is 3% relative and long term isothermal temperature stability is about 4% relative.

Samples, placed in the side arm of the furnace evacuated to 10^{-5} torr, are transferred to a crucible. Long preheating periods are required for graphite crucibles to attain low blanks. The use of tungsten crucibles avoids this difficulty but water in samples reacts with tungsten at high temperature to produce hydrogen. Evolved gases are transferred by a mercury diffusion ejection pump to a vacuum collection system consisting of a Baratron pressure monitor and a series of volume-calibrated glass bulbs for sequential gas collection. The pressure is recorded on a strip chart recorder. Total gas released is calculated using the pressure and bulb volume. Composition usually is determined by mass spectrometry. Gas chromatography also is used for larger quantities of collected gas.

The overall reliability of the system was measured using three NBS SRMs, two of hydrogen in titanium and one of oxygen in a steel. The results, for a heating period of 30 min at a constant temperature of 1500°C for the two hydrogen SRMs and 1700°C for the oxygen SRM, are given in Table AL 014-I. Quantitative recovery is indicated for both gases with a relative standard deviation of about 10%. The range of sample weights analyzed for SRM 352 was 80 to 400 mg, providing 2.5 to $13\text{ }\mu\text{g H}_2$, equivalent to 1.3 to 6.4 micromoles. The detection

limit, defined as the amount of sample to provide a measurement intensity equal to the overall background intensity (furnace plus mass spectrometer) for hydrogen at mass 2, is 10 nmol of hydrogen.

Recoveries and detection limits also were determined for eight gases (Table AL 014-II). For this evaluation, measured quantities of the gases except hydrogen and helium were injected into the cold furnace through a rubber septum using a gas-tight syringe. Hydrogen and helium were introduced into the furnace as prepared mixtures with argon in small volume-calibrated gas-tight containers. The detection limit has the same definition as previously, based on measurement of the most intense mass peak or the sum of peak intensities for polyisotopic gases.

The relatively high detection limits for hydrogen and helium are caused by low mass spectrometric sensitivity factors, and for nitrogen and carbon dioxide high backgrounds at the major mass peaks of 28 and 44. Accurate isotopic abundance determination of isotopes greater than 1% abundance for krypton and xenon requires $2\text{ }\mu\text{moles}$ of each gas, a 1000-fold greater quantity than the detection limit.

The next phase in this task is construction of equipment to measure the quantity and composition of released gas on a dynamic basis. A just-received rapid-scanning

TABLE AL 014-I
RELIABILITY OF GAS RELEASE
MEASUREMENT APPARATUS

NBS-SRM	NBS Value, wt%	Results, wt%		
		$\bar{y}$	s_i	n
352; H_2 in Ti	0.0032 ± 0.0002	0.0032	0.00028	8
354; H_2 in Ti	0.0215 ± 0.0006	0.0212	0.00150	5
356; O_2 in Alloy 6 Al 4 V	0.1332	0.1324	0.00150	5

TABLE AL 014-II
RECOVERIES AND DETECTION LIMITS
OF VARIOUS GASES

Gas	Recovery, %	Detection Limit nmol
H_2	88	8
He	88	1
N_2	88	4
O_2	86	0.2
Ar	96	0.01
CO_2	97	2
Kr	98	0.002
Xe	99	0.002

quadrupole mass spectrometer and a data-reduction system now on order will continuously analyze the released gas composition, and pressure will be continuously recorded.

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