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Progress Report

UC-79b (Base Technology)

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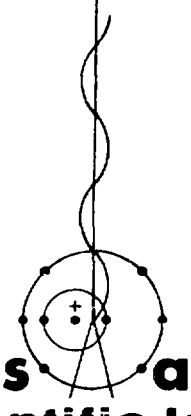
Examination of Fast Reactor Fuels, FBR Analytical Quality Assurance Standards and Methods, and Analytical Methods Development—Irradiation Tests

January 1—March 31, 1977

Compiled by

R. D. Baker



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ABSTRACT

This is the eleventh quarterly 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, K. E. Dowler, F. J. Fitzgibbon, M. E. Lazarus, J. M. Ledbetter, J. L. Lehmann, H. Martinez, P. A. Mason, F. H. Newbury, A. G. Nicol, J. A. Romero, T. J. Romero, D. S. Shaffer, L. N. Vikdal, W. T. Wood)

1. A device, see Fig. AL 001-1, was designed and fabricated for removal of the shroud tubes from sodium-bonded advanced fuel elements. The device was successfully used for removal of shroud tubes with a nominal wall thickness of 0.08 mm from two fuel elements during the last quarter.

The device, which includes a Unimat lathe, precisely cut through the cladding without damaging the shroud. Because of the sodium bond, the pin was heated during the removal operation. A center load was maintained on the fuel and shroud tube while maintaining a constant pull on the pin cladding of approximately 4.5 kg (10 lbs). The shroud tubes were ejected onto a receiving tray for further examinations.

2. Installation of two new ion etcher vacuum systems in the metallograph blister have been completed. The systems incorporate a roots-type pump with a rotary vane foreline pump. Gate valves were incorporated in the vacuum lines which automatically open when the pump-system is energized. The valves will also automatically close should the blister enclosure pressure become too

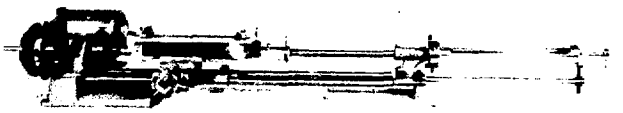

Fig. AL 001-1 Shroud Removal Device

negative due to a leaking ion etcher chamber. Both systems are presently being used in routine ion etching operations.

3. The new high-acid chemistry alpha box has been installed in the Wing 9 Hot Cell Facility. The box was installed in Cell 11 which was vacated by the former disassembly cell. Control consoles and ancillary equipment are presently being installed and operational checkout should begin next quarter.

4. The Programmed and Remote Systems (PaR) model 3000 bridge-mounted manipulator was installed in the east corridor at Wing 9. The manipulator replaced the General Mills model 300 manipulator which had deteriorated and replacement parts were unavailable.

5. The design and fabrication of a new unloading alpha box required to receive alpha contaminated shipments from Hot Fuels Examination Facility/North (HFEF/N) continued last quarter. A new transfer system has been designed to unload the Argonne National Laboratory/West (ANL/W) insert which will be used for T-2 cask shipments. The box will also contain the standard LASL transfer systems, an interim fuel element storage capability, and equipment required to perform preliminary examinations on fuel elements. A long-term storage capability is also being considered for installation underneath the alpha box.

6. A replacement analytical balance, used for immersion density measurements, was modified and installed in Cell 10 during the last quarter. The balance was upgraded from 0.2-mg sensitivity to 0.02-mg sensitivity by the Electrical Standards and Balance section at LASL. An immersion temperature monitor with digital readout to the nearest 0.01° C was also installed.

7. A new in-cell vacuum system, see Fig. AL 001-2, was designed and fabricated for the sectioning operation. This system collects the cutting into a throw-away container which is easily disconnected. The unit was designed for installation and removal through the 7-in. transfer system.

8. A new floor storage container was designed and fabricated for density and back-up burnup samples. The container can store up to 3°4 density samples or 900 burnup samples. It was designed for quick identification and recovery of the samples.

9. A new device was designed and fabricated which easily removes fuel from density samples up to 2.54 cm (1.00 in.) in length. The device has greatly decreased the fuel removel time previously required for this operation.

10. The computer program for the Optical Profilometer has been converted to the new LTSS System with the exception of the film and calcomp routines which are still not available with the system. Printouts and the magnetic output tapes can now be obtained with the new

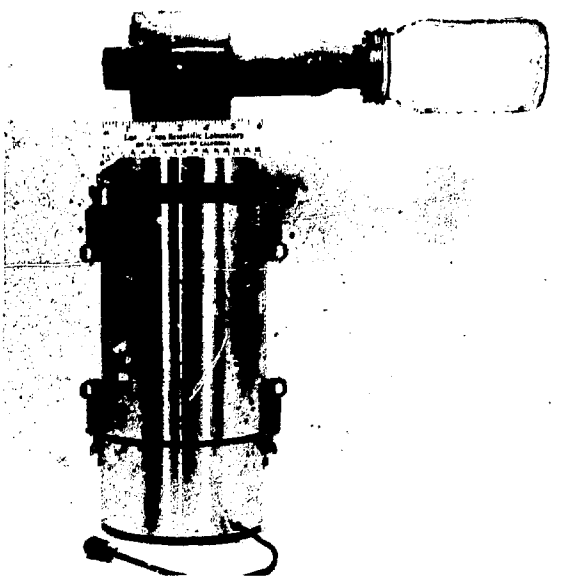

Fig. AL001-2. In-Cell Vacuum System

conversion. The Optical Profilometer data reduction program for HEDL and the "CHIT" Program for computation and printout of budget and pin status have also been converted.

B. Development Work and Maintenance of Manipulators

(A. L. Bridge, W. R. Carter, P. A. Mason, E. L. Mills, L. N. Vikdal)

1. The metallograph blister master-slave manipulators were overhauled during the shutdown for installation of the ion etcher vacuum systems.

2. A new seal configuration design for the master-slave, manipulator-boot, seal collar interface has been under test during the quarter. It is fabricated from a section of a hypalon dry box glove. This material is expected to extend the useful life of the seals in the hot cell environment and permit replacement of the butyl rubber inflatable inner tubes presently being used. The inner tubes have consistently developed leaks three to six months after installation in the hot cells due to exposure to high temperatures from installation near 400-watt mercury vapor lights.

3. Two CRL extended reach master-slave manipulators (models F and D) were obtained on loan from another LASL group. These are planned for installation at the end corridor operating station adjacent to the new unloading cell. The manipulators have been overhauled in anticipation of installation during the next quarter.

4. The seal packages inside two manipulator through-tubes were overhauled.

5. Two manipulators were removed from service for overhaul.

6. Six manipulator slave arm boots and seal collars were replaced during the quarter.

III. ANALYTICAL CHEMISTRY

A. Gamma Scanning

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

Most of the time available for development work in gamma scanning had to be devoted to equipment maintenance, procurement operations, and to updating computer programming codes to be usable with the new time-sharing computer system at the LASL. The equipment presently available are the original scanner, that is now obsolete and of limited applicability, and the more recent Nuclear Data 50/50 system in routine use. The original system is used as a back-up, temporary replacement for the Nuclear Data 50/50 system when the latter malfunctions, and also as an out-of-cell scanner for flux monitor wires. To keep the older system operating, a Ge(Li) crystal was reconditioned and upgraded to be compatible with the primary detector system. The crystal is now being used in this system to scan flux monitor wires from TREAT experiments.

The Nuclear Data 50/50 system, originally the best system available, is becoming obsolete and some replacement electronic components are no longer available. Purchase of an updated replacement system was started a few months ago but has been delayed because the system must be processed as Automatic Data Processing (ADP) equipment. This requires more extensive documentation and justification prior to purchase. Completion of the purchase request documentation should be accomplished early next quarter.

The LASL central computing facility (CCF) is changing operating systems from being batch oriented to time sharing. The Livermore Time-Sharing System (LTSS) is being implemented, requiring the conversion of all present codes to the new operating system. To date, the gamma-ray analysis program HPERMET[1] has been partly converted to LTSS and is operating, but there is one additional conversion to the extended FORTRAN compiler required in the future. Work is continuing on the conversion of the remaining programs with the completed conversion expected by the end of this fiscal year.

B. The Sealed-Reflux Dissolution System

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

The sealed-reflux dissolution system[2] is being redesigned to dissolve up to 100 g of $(U,Pu)O_2$ fuel samples.[3] For safety purposes, a pressure relief valve capable of operating in an acid atmosphere at 150°C was designed to release at pressures above 345-415 kPa (50-60 psi). This pressure relief valve permits the safe operation of the dissolution system which contains 450 ml of 13M HNO_3 and 10 drops of 12M HCl at 150°C and 275 kPa (40 psi). An alternate acid mixture

consisting of 450 ml of 6M HCl and 5 drops of 15M HNO_3 attains a pressure of 205 kPa (30 psi) at 150°C and can be used if an HCl medium is preferred to a HNO_3 medium.

C. Determination of Trace Carbon in Irradiated Materials

(J. W. Dahlby, M. A. Maez, H. J. Kavanaugh)

A method for determining trace carbon in irradiated materials is being developed by modifying an existing method that uses a manometric detection system for the evolved CO_2. To convert carbon in stainless steel cladding materials to CO_2 quickly, temperatures in excess of 1300°C are required. A platinum resistance furnace capable of attaining 1500°C was tested. The furnace permitted the release of carbon without the use of flux materials, but the furnace had only a short life due to the rapid volatilization of platinum metal at this temperature. Therefore, work with this type of furnace was discontinued.

An induction furnace system is currently being used where the sample is heated in contact with a flux material. This system has the disadvantage that the flux material contributes to the blank, but the blank can be controlled at a constant value by preigniting the crucible and accurately weighing the amounts of flux used in each run. The method was tested by analyzing two NBS Standard Reference Materials. For a steel material, the NBS certified content is 0.2%; we found 0.206% carbon with a relative standard deviation of 6%. For a stainless steel material, the NBS certified carbon content is 78 ppm; we measured 88 ppm carbon with a relative standard deviation of 7%. The method will be tested next on irradiated materials.

D. Determination of Oxygen Potential in Irradiated Oxide Fuels

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

The three probes for the oxygen-potential meter originally supplied by the manufacturer continue to malfunction. Three new probes have been ordered for the instrument with further testing delayed until their arrival.

IV. MICROSTRUCTURAL ANALYSIS

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

A new high-speed pumping system for the in-cell ion gun etching system was installed this quarter. A second ion gun etching system was also installed in the metallographic blister at the same time. The second ion gun etcher also incorporated the improved high-speed pumping system. The new pumping systems have been installed outside the radiation barrier so that maintenance will be simpler. These improvements will almost triple our ion gun etching capability.

V. REQUESTS FROM DRDD

Examination of Irradiated Materials

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

General Electric Company: Four irradiated fuel pins and three structural pins were received the second quarter of FY 1977. Examinations performed on 79 pins are listed in Table AL 001-I.

TABLE AL 001-I

POSTIRRADIATION EXAMINATIONS OF CAPSULES AND PINS FROM GE

	Examination	No. of Capsules or Pins Examined
1.	Visual Examination	18
2.	Preliminary Measurements	34
3.	Profilometry, Optical	19
4.	Radiography	25
5.	Gamma Scan, Gross	20
6.	Gamma Scan, Multispectral	20
7.	Photography, Full Length	18
8.	Photography, Incremental	18
9.	Eddy Current	22
10.	Sectioning	15
11.	Density Measurement Preparation	13 (14)[a]
12.	Microprobe Analysis	3 (5)
13.	Burnup Analysis	3 (6)
14.	End Cap Length Measurement	18
15.	EMX Preparation and Photography	5 (8)

[a] Numbers in parentheses in this and following tables refer to number of samples.

Hanford Engineering Development Laboratory: Forty-two irradiated fuel pins were received the second quarter of FY 1977. Examinations performed on 72 pins are listed in Table AL 001-II.

The following were shipped to HEDL during the second quarter of FY 1977: six irradiated archive standards; three irradiated fuel pins from the P 23 series; four irradiated fuel pins from the PNL-3 series.

Los Alamos Scientific Laboratory: Examinations performed on 20 irradiated fuel pins are listed in Table AL-001-III. These are carbide and nitride pins with the technical evaluation being carried out by LASL personnel under the Advanced Fuels Program. One pin was received during the second quarter of FY 1977.

TABLE AL 001-II

POSTIRRADIATION EXAMINATIONS OF CAPSULES AND PINS FROM HEDL

	Examination	No. of Capsules or Pins Examined
1.	Visual Examination	9
2.	Preliminary Measurements	9
3.	Radiography	9
4.	Gamma Scan, Gross	9
5.	Gamma Scan, Multispectral	9
6.	Gamma Scan, Fuel Column Length	9
7.	Gas Sampling and Analysis	10
8.	Photography, Full Length	9
9.	Photography, Incremental	18
10.	Wire Wrap Removal	18
11.	Sectioning	7
12.	Density Measurement	2 (6)
13.	Microprobe Analysis	2
14.	Two-Dimension Scan	4 (6)
15.	Split Pin Cladding	1
16.	Optical Microscopy[a]	4 (9)
17.	EMX Preparation and Photography	2

[a]The optical microscopy includes macrophotography, alpha-autoradiography, beta-gamma autoradiography, and as-polished and etched photomicroscopy (including mosaics) in inert (N_2) atmosphere. Specimens from other experimenters' fuel pins were examined in like manner.

TABLE AL 001-III

POSTIRRADIATION EXAMINATIONS OF CAPSULES AND PINS FROM LASL

	Examination	No. of Capsules or Pins Examined
1.	Profilometry, Optical	30[a]
2.	Profilometry, Spiral	8
3.	Profilometry, 20 Trace	3
4.	Radiography	1
5.	Gamma Scan, Gross	4
6.	Gamma Scan, Multispectral	4
7.	Two-Dimension Scan	1
8.	Gas Sampling and Analysis	5
9.	Photography, Full Length	8
10.	Photography, Incremental	12
11.	Photography, Kollmorgen	4
12.	Bonding Removal	1
13.	Wire Wrap Removal	4
14.	Eddy Current	4
15.	Sectioning	3
16.	Density Measurement	2 (9)
17.	Microprobe Analysis	4
18.	Burnup Analysis	4
19.	Retained Fission Gas Analysis	4
20.	Diameter Measurements, Micrometer	2 (3)
21.	Shroud Removal	2
22.	Clad Removal	1
23.	Na Distillation	2
24.	Clad Sectioning	2
25.	Clad Splitting	2
26.	Optical Microscopy	8 (30)
27.	EMX Preparation and Photography	3 (4)

[a]Includes 27 unirradiated fuel pins.

Westinghouse Advanced Reactor Division: Examinations conducted on 14 irradiated fuel pins are listed in Table AL 001-IV. No fuel pins were received the second quarter of FY 1977.

Two irradiated fuel pins from the W3 series were shipped to HEDL and 17 split tube samples from the W3 and W4 series were shipped to ANL-W during the second quarter of FY 1977.

TABLE AL 001-IV

POSTIRRADIATION EXAMINATIONS OF CAPSULES AND PINS FROM WARD

Examination	No. of Capsules or Pins Examined
1. Density Measurement	9 (35)
2. Burnup Analysis	5
3. Optical Microscopy	9 (48)

Argonne National Laboratory: Examinations conducted on one irradiated fuel pin are listed in Table AL-001-V. One fuel pin was received the second quarter of FY 1977.

VI. QUALITY ASSURANCE
(L. E. Lanham)

Analytical Chemistry

1. A sample preparation procedure has been written to carry out the requirements of the Advanced Fuels, fuel pellet sampling plan. The analytical chemistry dry box operations for sample preparation have been reviewed by Quality Assurance (QA), the procedure has been approved, and the documents are now a part of the QA system.

2. Two procedures were reviewed, approved, and released for use on applicable QA programs.

3. One purchase order was reviewed and released to procurement.

4. The documentation for two shipments was reviewed by QA and the shipping request was released to the shipping department.

TABLE AL 001-V

POSTIRRADIATION EXAMINATIONS OF CAPSULES AND PINS FROM ANL

Examination	No. of Capsules or Pins Examined
1. Visual Examination	1
2. Preliminary Measurements	1
3. Profilometry, Optical	1
4. Radiography	1

Hot Cell Operations

1. The review of the sectioning operation has been completed. QA and technical management have agreed on the findings and they have been implemented.

2. The review of the cell atmosphere monitors is in process.

3. QA has requested that maintenance operations for the vacuum pump in the sodium distillation cell be reviewed. At the present the pump is under the cell floor, which makes maintenance difficult and costly.

4. Eleven procedures were reviewed by QA and approved for use in QA programs.

5. One purchase order was reviewed and released to procurement.

6. The documentation was reviewed on seven shipments.

Microstructural Analysis

1. An audit was conducted for operations, equipment, and documentation in microstructural analysis. A meeting was held with t rincipal Investigator to discuss the audit findings. A written response was prepared and made a part of the audit report. The audit report has been approved by the Program Manager.

2. Four procedures were reviewed and approved for use in QA programs.

3. One purchase order was reviewed and released to procurement.

VII. REFERENCES

1. G. W. Phillips and K. W. Marlow, "Program HYPERMET for Automatic Analysis of Gamma-Ray Spectra from Germanium Detectors," NRL Memorandum Report 3198 (January 1976).

2. J. W. Dahlby, R. R. Geoffrion, and G. R. Waterbury, "The Sealed-Reflux Dissolution System," Los Alamos Scientific Laboratory report LA-5776 (January 1975).

3. R. D. Baker, "Examination of Fast Reactor Fuels, FBR Analytical Quality Assurance Standards and Methods, and Analytical Methods Development-Irradiation Tests," July 1 - September 30, 1976, Los Alamos Scientific Laboratory report LA-6586-PR, p. 2 (November 1976).

PROJECT A L 003

FBR ANALYTICAL QUALITY ASSURANCE STANDARDS AND METHODS

RESEARCH AND DEVELOPMENT

Person in Charge: R. D. Baker
Prir ipal 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, (4) the preparation of continuously updated analytical method manuals, and (5) maintenance of referee analysis capabilities to characterize, on a reimbursable basis, materials in dispute between fabricators (vendors) and reactor operators (purchasers). 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. CALIBRATION AND QUALITY CONTROL MATERIALS (F. R. Roensch, J. E. Rein)

As a major continuing task, calibration and quality control materials of uranium oxide and plutonium oxide (the source materials used to manufacture the mixed oxide fuel for the FTR) and of mixed oxide were distributed to Babcock and Wilcox (B & W), Apollo, PA, as the vendor of the FTR fuel and to the Hanford Engineering Development Laboratory (HEDL) as the reactor operator. At the request of HEDL, the shipment of materials now being prepared will include materials for the General Electric-Vallecitos (GE-V) facility for the first time. HEDL has contracted with GE-V to manufacture experimental fuel pins containing mixed oxide fuel with essentially the same chemical specifications as the FTR fuel. The source materials and fuel will be chemically analyzed at GE-V and at HEDL under quality assurance surveillance similar to that for the FTR fuel.

At the request of B & W, approved by HEDL and the ERDA Hanford Operations Office, a lot of plutonium oxide was characterized for plutonium isotopic distribution to be used by B & W for calibration of the mass spectrometric measurement. B & W finds that the isotopic distributions of the three Standard Reference Materials (SRM 946, 947, and 948) available from the National Bureau of Standards (NBS) do not match the isotopic distribution of the plutonium in FTR mixed oxide fuel sufficiently closely to provide accurate calibration of its mass spectrometric measurement. The isotopic distribution of the specially characterized PuO_2 lot meets FBR fuel specifications. This material will be included in the next shipment to B & W. Also provided will be a tabulation of the changing plutonium isotopic distribution as a function of time, adjusted for plutonium isotope decay.

Reanalysis of three lots of mixed oxide powder that had been packaged as 1-gram quantities in individual glass vials for use in the Safeguards Analytical Laboratory Evaluation (SALE) program showed storage instability. As this change in composition bears on the stability

of these materials and their effectiveness as standards, the details are being included here. A significant, among-vial difference existed in the uranium and plutonium assay values in previously homogeneous powder. Variable weight changes were obtained on heating the powder to constant weight at 120°C. Most of the samples gained weight. An investigation is under way to determine the cause of instability. Also, mixed oxide pellets used as quality control samples for the FTR quality assurance program are being overchecked for uranium and plutonium assay contents to establish their storage stability.

HEDL has placed an apparatus into operation to remove fluoride by pyrohydrolysis from a lot of PuO_2 that then should be sufficiently pure to be used as the matrix material to prepare calibration and quality control blends of nonmetal impurities. HEDL reports that a lot of PuO_2 that appears suitable as matrix material to prepare calibration and quality control blends of metal impurities will be shipped soon.

Atlantic Richfield Hanford Company (ARHCO), the normal producer of plutonium oxide that is used as the plutonium source material for the manufacture of the FTR mixed oxide fuel, has not resumed production. LASL is serving as the alternate producer, using a special process line including pyrohydrolytic removal of fluoride and chloride. Each produced lot is being extensively analyzed for chemical specifications, including plutonium assay content, plutonium isotopic distribution, ^{241}Am, carbon, chloride, fluoride, nitrogen, phosphorus, sulfur, 28 metal impurities, and trace uranium. Perhaps some of this PuO_2 may be adequately pure to be used in preparing quality control materials.

III. ANALYTICAL METHOD DEVELOPMENT

A. Determination of Plutonium

(D. D. Jackson, R. M Hollen, F. R. Roensch, J. E. Rein)

A specific, precise, controlled-potential coulometric method for plutonium is being developed, using an apparatus consisting of a high-precision potentiostat controlled by a desk-top programmable calculator. The working electrode is platinum gauze, and the electrolyte is 5.5M HCl-0.015M sulfamic acid. The electrochemical analysis sequence is a reduction at 0.25V vs standard calomel electrode (stated potentials in this report are on this basis) to produce Pu^{3+}, a preliminary oxidation at 0.57V, at which potential many ions oxidize but plutonium does not, addition of phosphate, which lowers the Pu^{3+}-Pu^{4+} half-cell potential, and a measurement oxidation of Pu^{3+} to Pu^{4+} at 0.68V. Measurement precision at the 5-mg plutonium level is 0.1% relative standard deviation. Time of analysis is about 30 min. An extensive investigation of the effects of diverse ions is under way. At this time, none of the impurities normally in mixed oxide fuel have been found to interfere. At least five times as much uranium as plutonium can be tolerated. Long-term stability of the electrode system has been excellent and the calibration factor (amperes/mole of plutonium) stays constant over several-month, time spans.

B. Ion Exchange of Elements in Hydrobromic Acid, Hydroiodic Acid, and Strong Nitric Acid

(S. F. Marsh, J.A. Alarid, M. McLeod, C. F. Hammond, J. E. Rein)

Three ion exchange systems are being investigated: (1) cation exchange in strong nitric acid, (2) anion exchange in hydrobromic acid, and (3) anion exchange in hydriodic acid. The distributions of 58 elements were determined for each system for three resins, macroporous, 4% cross-linked divinylbenzene (DVB), and 8% cross-linked DVB, for a wide range of acidities. Many separations of apparent usefulness to the analytical chemistry of FBR fuels and other reactor components were obtained. Results are being compiled and will be reported later.

C. Determination of Sulfur

(D. J. Temer)

The present method for determining sulfur in mixed oxide fuel requires the tedious dissolution of the sample and a distillation separation, which are time-consuming. Analysis of the solid sample without dissolution, therefore, offers considerable cost savings in avoiding the chemical steps. To attain these goals, a commercial sulfur analyzer was purchased, installed, and operationally tested. Application to the analysis of the fuel materials and other reactor samples is in progress.

Bench top testing of the Dohrmann-Envirotech sulfur analyzer has produced encouraging results. Several

quality control blends, consisting of a uranium oxide matrix doped with bismuth sulfate, were analyzed for sulfur, and the results correlate very well with the theoretical make-up of the blends. Also, good recovery was obtained when sulfur was determined on a NBS electrolytic iron standard. It was necessary to use a flux material in the analysis of the electrolytic iron.

The furnace assembly of the analyzer was redesigned to increase its size and thereby permit use of a flux with the sample. The new design also improves capability for insertion of the furnace and maintenance operations in a containment box. This new furnace assembly is currently being tested.

IV. ANALYTICAL METHOD MANUALS
(G. R. Waterbury and Staff)

Document RDT F11-2 "Analytical Chemistry Methods for Boron Carbide Absorber Material" was prepared by HEDL to supersede the original RDT Standard RDT F11-2T of July 1973. The revision, containing new and modified methods, was reviewed, and detailed comments were transmitted to HEDL.

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, various gases, and trace impurities in irradiated fuels.

The tasks in this program include the development of (1) burnup methods based on chemical separation-thermal ionization mass spectrometry, on rapid chemical analyses using inexpensive apparatus, and on isotope-dilution spark-source mass spectrometry, (2) methods for the measurement of gases and their release rates as functions of temperature and time, and (3) improved, spark-source mass-spectrometric methods for determining minor and trace elements in irradiated reactor materials. Longer range tasks include (1) prooftesting of burnup methods and preparing burnup reference materials jointly with ACC-Idaho, and (2) developing apparatus, techniques, and methods for isotope-dilution, spark-source mass-spectrometric determination of relative fissions of fissioning nuclides, for measurements of release of fission products of lower volatility than krypton and xenon, and for new instrumental determinations of trace and minor constituents in irradiated fuels.

II. DETERMINATION OF BURNUP

Previously developed methods use either chemical separation-thermal ionization mass spectrometry or low-expense chemical separation-spectrophotometry to determine reactor fuel burnup. Inexpensive chemical techniques that provide higher precision than spectrophotometry and techniques that use spark source mass spectrometry are being developed.

A. Chemical Techniques Using Inexpensive Apparatus

The first chemical procedure developed using low-cost apparatus incorporated ion exchange resin separation of uranium, plutonium, and total rare earth fission products (as the fission monitor) followed by spectrophotometric determination of each.[1] Two other analysis techniques are being investigated.

1. Complexometric Titrimetry

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

One technique being investigated is a microcomplexometric titration of total rare earth fission products (as the fission monitor), uranium, and plutonium. As previously reported, titrations of 56-nmole quantities of a mixture of rare earths, simulating FBR fission products, with ethylenediaminetetraacetic acid (EDTA) had a relative standard deviation of 1%. A copper-selective electrode and an indicator of equimolar Cu-EDTA were used to detect the endpoint.

As UO_2^{2+} does not form highly stable chelates, a procedure was developed in which uranium is reduced to U^{4+} on a lead reductor column of 0.1 M HCl and titrated with diethylenetetraminepentaacetic acid (DTPA) to a visual end point with xylenol orange as the indicator. The titration portion of the procedure is a modification of that proposed by Rykov et al.[2] A quantity of 0.5 micromole of uranium has been determined with 2% relative standard deviation. Refinements in technique are expected to improve the precision to at least 1% relative standard deviation.

Plutonium reduces on a lead reductor column to Pu^{3+} which neither forms a colored complex with xylenol orange nor is titrated with DTPA in 0.1M HCl. At higher pH values, Pu^{3+} forms stable complexes with xylenol orange and DTPA, but so does the Pb^{2+} that elutes from the reductor column. Experiments were unsuccessful to establish a system in which a colored complex of Pu^{3+} was titratable with a chelon without interference from metal ions from the reductor column. Combinations evaluated were reductants of lead, zinc, and cadmium; colored complexes of xylenol orange, arsenazo I, and arsenazo III; and DTPA as the chelating agent.

Potentiometric end-point detection was investigated for the chelometric titration of plutonium, using sensing electrodes of mercury, gold, and gold-amalgam and an equimolar mercury-chelon complex described by Reilley et al.[3] Initial experiments were with Nd^{3+} to simulate Pu^{3+} and with DTPA as the titrant. Of the three sensing electrodes, the gold-amalgam provided the largest and most reproducible potential change at the end-point. It, therefore, was used for subsequent potentiometric titrations.

The initial technique used for the end-point measurement was the second derivative computation for equal titrant additions. End points were erratic, varying with addition size and elapsed time between additions. Improved precision was gained by using a slow continuous titrant addition and continuous measurement of the potential. An automated potentiometric titrator was constructed from low-cost components in which titrant is delivered by a Digipet micrometer-screw pipet, driven by a 2-rpm motor, at a rate of 1 ml per 16 min and the potential change with time is plotted on a strip-chart recorder. The graphic end-point, determined as the maximum change in slope, was significantly more reliable than the previous manual method. The linear least squares fit for quadruplicate titrations of six neodymium levels over the range of 0.0175 to 0.105 micromole was excellent. The relative standard deviation was less than 0.5%.

Method development for plutonium was undertaken using this titration apparatus, DTPA titrant, Hg^{2+}-DTPA complex indicator, a saturated potassium sulfate reference electrode, and the gold-amalgam electrode. A commercial mercury ion electrode, tested as a possible replacement for the gold-amalgam electrode, gave smaller potential changes and was abandoned. Various reductants to produce Pu^{3+} were evaluated first in titrations of neodymium. If the titration of neodymium was successful, the test was repeated with plutonium. Hydroxylamine nitrate, hydrazine hydrosulfate, hydrazine formate, and semicarbazide nitrate, all prepared by converting the chloride or hydroxide forms, gave satisfactory end points with neodymium but not with plutonium. Both sodium sulfite and mixed sulfamic acid-ascorbic acid interfered with the titration of neodymium. This interference is attributed to a reaction of the reductant with the Hg^{2+}-DTPA indicator. Reilley et al.[3] state that this type of titration is successful with ions that form a weaker complex than the Hg^{2+}-chelate indicator. Our experiments to date have verified this statement. Because the stability of the Pu^{3+}-DTPA complex is considerably lower than that of the Hg^{2+}-DTPA complex, and the Pu^{4+}-EDTA stability is much higher, the reductants may have failed to maintain the plutonium as Pu^{3+} in the presence of DTPA.

A variation of this titration is being investigated in which plutonium in the 4+ valence state is titrated. This requires the use of a very strong indicator complex which, for DTPA, appears limited to Tl^{3+}, Bi^{3+}, and possibly In^{3+}. A suitable electrode system that responds to these ions must first be developed.

2. Liquid Chromatography
(W. D. Spall, M. R. Ortiz, S. F. Marsh)

Another chemical burnup technique under study is liquid chromatography which can provide high sensitivity and can measure the fission product monitor (such as rare earths), uranium, and plutonium in a single analysis. A liquid chromatograph was constructed in which the sample and eluting agents contacted only glass, Teflon, and Kel-F which are inert to a variety of organic solvents as well as high-halide aqueous media. The detector is a commercial flow-through spectrophotometer which, for detecting total rare earths (as the fission monitor), uranium, and plutonium, requires sensitive color complexes formed with organic complexants. A

ion; or term objective is development of detectors having specificity for inorganic ions enabling use of versatile ion exchange columns with aqueous media.

Experiments are in progress to establish a combination of organic complexant, column material, and mobile phase that provides separated fractions of total rare earths and of uranium or plutonium separately or together. Initial success has been attained for arsenazo III complexes using a 30-cm column of C_{18}-porasil and a mobile phase of a water-diethylamine mixture. Unreacted arsenazo III, the Nd^{3+}-arsenazo complex, and the U^{6+}-arsenazo complex were separated. The system will be tested for separating total rare earths and plutonium after a further evaluation of the composition and flow rate of the mobile phase and the column length to attain greater resolution. Solvent pump leakage has been a problem and systems that should be more reliable are on order.

Commercial ion-selective electrodes are not available for uranium, plutonium, or major fission product groups such as the rare earths. Efforts to develop ion-selective electrodes for uranium have included investigation of a variety of polymeric membranes containing selected insoluble salts, ion exchange resins, metal complexes, and liquid ion exchangers as the electrode sensing surface. Stable, reproducible response has not yet been obtained. A technique for determining active transport phenomena across the membranes has been developed to assist in understanding the mechanisms involved.

Electrodes fabricated from U-Ti, U-Mo, and U-Nb alloys gave a measurable response superimposed on a large baseline drift. These alloys, while less reactive than uranium metal, still are too reactive for use in acid media. Electrodes using sensing surfaces of ceramic grade UO_2, U_3Si_2, and US_2 did not respond to changes in uranyl ion concentration.

3. Oxidation of Plutonium by Fuming Perchloric Acid

(D. D. Jackson, S. F. Marsh, F. R. Roensch, R. M. Abernathey, J. E. Rein)

The thermal ionization mass spectrometric determination of burnup, based on measurements of ^{148}Nd as the fission monitor and of the residual uranium and plutonium, is preceded by a chemical treatment that produces separated fractions of neodymium, uranium, and plutonium. One step in the chemical separation[4] used in our laboratory involves fuming the mixture of sample plus ^{150}Nd-^{233}U-^{242}Pu internal standard with HF and $HClO_4$ to dissociate any plutonium polymers and oxidize plutonium to Pu^{6+}. Oxidation to Pu^{6+} produces chemical identity of sample plutonium and added ^{242}Pu isotopes, and therefore, no isotopic fractionation, and prepares the sample for ion exchange resin separation.

This separation procedure also precedes the chemical burnup determination based on spectrophotometric measurement of total rare earths, uranium, and plutonium,[1] and is being considered as the treatment prior to complexometric titration measurements. For these measurements, quantitative recovery of plutonium is necessary, and the fuming with $HClO_4$ must quantitatively oxidize plutonium.

Recent experiments showed that the residue formed upon fuming hydrochloric-perchloric acid solutions of Pu^{3+} to dryness at 160°C produced an effective plutonium oxidation state of about 3.5 and no Pu^{6+}. If HNO_3 were present also, or if the $HClO_4$ fuming were stopped before the acid was completely evaporated, the plutonium valence was about 5.6, equivalent to 80% Pu^{6+} and 20% Pu^{4+}. Plutonium was oxidized completely to Pu^{6+} when fumed with $HClO_4$ at 200°C and remained so even in the baked residue. Fuel samples analyzed for burnup in our laboratory always contain HNO_3, and fuming at temperatures below 200°C should produce dynamic equilibrium and isotopic exchange.

B. Spark Source Mass Spectrometry

(R. M. Abernathey, C. F. Hammond, W. D. Spall, J. E. Rein)

A program is under way to develop burnup methods using a spark source mass spectrometer to determine accurately and rapidly a fission product monitor (such as neodymium), relative to uranium and plutonium by isotope dilution with a triple ^{150}Nd-^{233}U-^{242}Pu spike. This will provide a total atom percent fission measurement. Immediate emphasis is on photoplate detection. To attain maximum reliability, an extensive emulsion calibration is in progress. Various isotope pairs are being evaluated as step ratios using a wide range of exposures and

careful densitometry of line densities. A recording integrator was custom fabricated for the densitometer to provide optional integrated outputs of transmittance, absorbance, and Seidel function for each line scanned. These outputs are produced concurrently with the normal output of differential transmittance that is plotted on a strip chart recorder. Plates prepared for emulsion calibration have been scanned and comparison of the various output modes of data collection is in progress. The "best" settings of scan speed, slit width, slit height, and geometrical orientation of the line relative to the slit have been established.

This project has been delayed about six weeks by malfunctioning of the spark source mass spectrometer.

III. DEVELOPMENT OF GAS MEASUREMENT TECHNIQUES

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

The second apparatus being developed in this task is for the dynamic measurement of various gases released from materials under programmed cycles of temperature and time. It consists of a quadrupole mass analyzer attached to an inductively heated vacuum furnace, under control of a temperature-time programmer, and a batch inlet system for admitting pure gases for pressure calibration or for internal standard calibration during an experiment. A data acquisition system interfaced to the mass analyzer and the associated computer programs provide high-speed data output and reduction which facilitate computation of gas measurement quantities.

The quadrupole mass analyzer was calibrated for 11 gases, H, He, CH_4, Ne, N, O, Ar, CO_2, SO_2, Kr, and Xe. The sensitivity factors were quite stable for all 11 gases, being about 3% relative standard over time periods of a day. Longer term stabilities are being determined. The detection limit for most gases is about 1 μmole per sec.

The control system for the inductively heated furnace is being modified to extend accurate control to lower temperatures. The present range is 500 to 2500°C. A switchable transformer will provide a lower range of 100 to 1800°C. An infrared pyrometer will be used to provide accurate temperature measurements.

IV. REFERENCES

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