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Examination of Fast-Reactor Fuels and FBR Analytical Quality-Assurance Standards and Methods

October 1—December 31, 1980

University of California

LOS ALAMOS SCIENTIFIC LABORATORY

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EXAMINATION OF FAST REACTOR FUELS AND FBR ANALYTICAL
QUALITY ASSURANCE STANDARDS AND METHODS

October 1—December 31, 1980

Compiled by
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ABSTRACT

This is the twenty-fifth quarterly report on the Examination of Fast Reactor Fuels and Fast Breeder Reactor (FBR) Analytical Quality Assurance and Methods at the Los Alamos National Laboratory.

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

PROJECT AL-001

EXAMINATION OF FAST REACTOR FUELS

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Principal Investigators: W. T. Wood
E. C. Walter
G. R. Waterbury

I. INTRODUCTION

This project is directed toward the examination and comparison of the effects of neutron irradiation on Liquid Metal Fast Breeder Reactor (LMFBR) Program fuel materials. Unirradiated and irradiated materials will be examined as requested by the Reference Fuels System Branch of the Division of Reactor Research and Technology (DRRT). Capabilities have been established and are being expanded for providing conventional pre-irradiation 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 DRRT.

Characterization of unirradiated and irradiated fuels by analytical chemistry methods will continue, and additional methods will be modified and mechanized for hot-cell application. Macro- and micro-examinations will be made on fuel and cladding, using the shielded electron microprobe, emission spectrography, 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 burn-up 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

(G. R. Brewer, B. M. Campbell, J. H. Cook, K. E. Dowler, F. J. Fitzgibbon, M. E. Lazarus, J. M. Ledbetter, T. J. Romero, W. T. Wood)

1. The Materials Science Division (MSD) of Argonne National Laboratory and Group CMB-11 of Los Alamos National Laboratory requested an attempt be made to reclaim the HC4A inner capsule and the irradiated fuel element. The HC4A is an advanced fuel TREAT experiment co-sponsored by MSD and CMB-11. The irradiated fuel element had mistakenly been assembled upside down in the inner capsule.

The HC4A inner capsule was shipped to CMB-14 from the Hanford Engineering Development Laboratory and transferred into the Wing 9 Hot Cell Facility. Four remote machining operations on the inner capsule were required to reclaim the capsule hardware and the irradiated fuel element. The fuel element was then inspected by visual, radiography, and gamma scanning techniques and there was no apparent damage. The inner capsule was refurbished by CMB-11. The fuel element and inner capsule were then shipped to HEDL for reassembly.

The remote disassembly of the HC4A was accomplished by using a Hardinge Lathe which is remotized for hot cell use. The first machining cut removed the base face (end cap) from the inner capsule. With the base face removed, the NaK loading shut-off valve was accessible and the NaK

was drained from the inner capsule. The heat sink pedestal support and heat sink pedestal base were drilled and pinned together to protect the fuel element during the final stages of machining. In 16 passes, the diameter of the heat sink pedestal base was reduced 0.635 cm (0.250-in.). With the diameter reduced, a parting tool was used to come in from the bottom of the pedestal base and machine away the weld that joined the heat sink pedestal support and pedestal base. The pin that had earlier been inserted to hold these two components together was then removed and the fuel element withdrawn from the inner capsule. A photograph taken after the final cut is shown in Fig. AL 001-1.

FIG. AL 001-1.
HC4A Inner Capsule Disassembly.

2. Modifications for the Wing 9 Hot Cell Facility to accept full length FFTF fuel pins continues. Two connecting alpha-boxes to be installed in Cells 2 and 4 so the new T-3 shipping cask can be unloaded directly into the cells have been received. Fabrication of the cell-cask interface glovebox and shielding is about 50 percent complete. Quotations have been requested for

fabrication of an air bearing cart for moving the T-3 cask from the transporter to the cell-cask interface box. The design and fabrication of auxiliary and examination equipment continued last quarter.

3. The replacement alpha-box for Cell 9 has been fitted with its mechanical and electrical equipment, the interior painted, and the complete box successfully helium tested. The old alpha-box was removed from Cell 9 last quarter, crated, and then transferred to the waste disposal area. The new box has been temporarily placed in Cell 9 for a fit-check, alignment, and to evaluate re-designed equipment. The Kollmorgen window has been canted to permit viewing areas of the box which were obscured before. The main viewing window has a second sealed pane installed as a backup. Should the inner pane or seal develop a leak, the alpha-box can continue to function fully with no impact to operations. The pneumatic system for Cell 9 has been replaced with an improved system designed for ease-of-repair and reliability. Also, the atmosphere pressure controls for both Cell 9 and 11 have been replaced with newer controls.

4. Samples of profilometry data processed on the group's Eclipse computer are being sent to each of the experimenters. The same data has also been processed at the Los Alamos CCF (Central Computer Facility) so that each experimenter can decide whether the Eclipse processed data is acceptable. The CCF processed data is plotted and presented on magnetic tape at 0.01 inch longitudinal increments, as compared to 0.02 inch longitudinal increments on the Eclipse. The profilometry data from the CCF is sent to each experimenter, on magnetic tape in a wide choice of character codes (6 bit ASCII, 8 bit ASCII, EBCDIC, BCD, BINARY) and a choice of magnetic tape formats (7 track, 9 track, 556 BPI, 800 BPI, or 1600 BPI). Magnetic tape data from the Eclipse will be available only in 8 bit ASCII, on 9 track 800 BPI tape. This configuration should be useable by all the experimenters and would greatly simplify our data processing.

5. The Cell 16 Laser Optical Profilometer is not operational because of two electrical problems which occurred last quarter. The first

problem causing the longitudinal stepping motor to stop before the stop-set point has been corrected. The second problem causing periodic additional pulses in the stepping motor circuit may be due to a problem in the Techmet Laser-Mike and the instrument may have to be returned to the factory for repairs.

Additional work to be done on the Cell 16 Profilometry System is to provide electronic switching between the mechanical and optical profilometers, and the data acquisition system. The electronic switch will also provide an extra input for another device to be added at a later date.

B. Development Work and Maintenance

(G. R. Brewer, B. M. Campbell, J. H. Cook, K. E. Dowler, F. J. Fitzgibbon, M. E. Lazarus, J. M. Ledbetter, T. J. Romero, W. T. Wood)

1. Four master slave manipulators required major overhauls last quarter.

2. Eight master slave manipulators required minor repairs.

3. Seven new seal packages and boots were installed.

4. The shoulder assembly was replaced on the General Mills rectilinear manipulator.

5. The remotized Zeiss metallograph installed in the Cell 8 blister has shown excessive transverse movement when the stage is rotated. To correct this, the stage support and positioning parts have been redesigned and are presently being modified.

III. ANALYTICAL CHEMISTRY

A. Gamma Scanning

(B. K. Barnes, A. S. Murray, and J. N. Quintana)

The new ND6620-based data acquisition and control system for the gamma scanner has proved to be reliable with only approximately 5% unscheduled down-time, due to hardware and software problems. Improvement and modifications are continuing to be made. The backup MIK-II, CAMAC crate controller has been strapped and tested. It functions except with one of the CAMAC modules. The reason why this particular module works with one of the CAMAC crate controllers but not with

the other is being investigated.

The new RL02 disk units have been installed on the PDP-11/40 and are operating well. The increased (10 mb) storage allows longer continuous Versatec plots than were previously possible. A telephone modem and the rewritten "HELPER" package have also been installed on our PDP-11. This allows the PDP-11 to act as a CCF terminal and to transmit files from the CCF to the PDP-11 and vice-versa. It should also allow direct link file shipping between our PDP-11/40 and our ND6620. Problems still exist with the link, however, and are being studied.

The previously reported new version of TWODIM is being compared to a filtered back projection reconstruction algorithm^{1,2} and to a maximum entropy iterative reconstruction technique.^{3,4} The reconstruction techniques tend to be some what heuristic as it has been proved that a nontrivial picture cannot be uniquely determined from its projection.⁵ Hence, an analytical measure of reconstruction performance is not possible. Preliminary results, however, tend to indicate that the modified filtered back projection technique with interpolation of our two measured projections to a much larger number of projections produces the best results for our typical data. Test data are now being taken on a trial fuel pin.

B. Determination of Burnup

Development of Chemical Method Using Complexometric Titrimetry

(S. F. Marsh, D. J. Hoard, J. E. Rein)

Chemical separation of uranium, plutonium, and either neodymium or total rare earths (as the fission product monitor), and their measurement by thermal ionization mass spectrometry or spectrophotometry are currently used to determine burnup. The mass spectrometric method is precise, but time consuming and expensive. The spectrophotometric method is faster and less expensive, but less precise. A method is being developed that involves chemical separation of uranium, plutonium, and total rare earths followed by their measurement by microcomplexometric titrimetry with an objective relative standard deviation of 2%. Procedures developed previously for determining plutonium and total rare earths

involve titration of their colored xylenol orange complexes with diethylenetriaminepentaacetic acid to release the xylenol orange, which has a color different from the metal complex. An automated titration apparatus, developed for these titrations, as well as for the titration of uranium discussed below, has been described.^{6,7}

The microcomplexometric titration method⁷ developed for uranium has the special advantage of titrating the stable U(VI) ion. The U(VI) arsenazo I complex is titrated with pyridine-2,6-dicarboxylic acid in hexamethylenetetramine-buffered medium of pH 4.9. Cyclohexanediaminetetraacetic acid and diethylenetriaminepentaacetic acid masking agents provide high tolerances for metal and nonmetal ions, including any expected to be present in the separated uranium fraction. The tolerances for 45 metal ions and 19 nonmetal anions have been reported.⁷

Development of a separation procedure is continuing. A promising reagent is dihexyl-N, N-diethylcarbonylmethylenephosphonate (DHDECMP), reported⁸ to extract plutonium and uranium strongly, rare earths and americium moderately, and most other metal ions slightly or not at all. Extraction chromatographic columns of DHDECMP coated on porous polymer beads are being investigated.

Distributions of uranium, plutonium, americium, and rare earths (using Eu(III)) have been measured for HNO_3 , HCl , and HClO_4 over an acidity range of 0.1 to 8M. The distribution coefficient (K_d) values in HClO_4 for U(VI), Pu(IV), Am(III), and Eu(III) are greater than 500 over the entire acidity range, thereby offering no separation usefulness. In HNO_3 , (Fig. AL 001-2) a maximum separation is attainable at 7 to 8M acidity, but americium and the rare earths will be in the same fraction. In HCl , (Fig. AL 001-3) only the separation of uranium from the other three elements is obtained for the acid range of 0.1M to 8M. Extrapolation of the data indicate a possible useful separation at higher HCl concentrations.

FIG. AL 001-2. Distribution Coefficients U(VI), Pu(IV), and Eu(III) Into DHDECMP From HNO_3 .

FIG. AL 001-3. Distribution Coefficients of U(VI), Pu(IV), Am(III), and Eu(III), Into DHDECMP From HCl .

C. Development of Gas Measurement Techniques
(J. W. Early and R. M. Abernathy)

Dynamic measurements of gases released from FBR fuels, cladding, and other reactor components as a function of temperature and time are used in investigations of material stability. An apparatus, consisting of a vacuum induction furnace, temperature-time programmer, and a quadrupole mass spectrometer, has been developed as a prototype for hot-cell measurements on irradiated materials.

Successful measurements of krypton and xenon isotopes and several other gases at parts-per-million concentration levels in UO_2 pellets have been made. Component additions are now being made for glove-box operations on uranium-plutonium fuel pellets.

The single-flow water cooling system on the furnace is being replaced with a system having a sealed primary loop, a heat exchanger, and a secondary cold water flow. Filters with nominal 5-micrometer pores were installed on the vacuum lines between the furnace inside the box and the pumps located externally to protect the pumps. Tests have shown that these filters do not significantly affect the response of the mass spectrometer to a gas release in the furnace. The response time is one to two seconds which is adequately short relative to a planned mass scan rate of about two minutes. Based on operating experience, several furnace components have been modified for increased operational life. The glove-box installation is essentially complete and test analysis of mixed oxide fuel pellets will start shortly.

An interface was designed and fabricated that will automatically switch mass spectrometer gains for seven scales at decade intervals from 10^{-5} to 10^{-11} A. The necessary minicomputer program has been developed.

IV. REQUESTS FROM DRRT

Examination of Irradiated Materials

(R. M. Abernathy, B. K. Barnes, J. H. Cook, J. W. Dahlby, K. E. Dowler, M. E. Lazarus, R. A. Morris, G. R. Waterbury, E. C. Walter, W. T. Wood, L. C. Michaels)

General Electric Company: No irradiated fuel elements were received from General Electric (GE) during the first quarter of FY 1981. Examinations performed on irradiated fuel elements are listed in Table AL-001-I.

Hanford Engineering Development Laboratory: Three irradiated fuel pins were received from the Hanford Engineering Development Laboratory (HEDL) during the first quarter of FY 1981. Examinations performed on irradiated fuel pins are listed in Table AL-001-II.

Los Alamos National Laboratory: This section contains carbide and nitride pins the technical evaluation of which is carried out by Los Alamos National Laboratory personnel under the Advanced Fuels Program.

Eight irradiated fuel pins were received from the Los Alamos National Laboratory during the first quarter of FY 1981. Examinations performed on irradiated fuel pins are listed in Table AL-001-III.

Westinghouse Advanced Reactor Division: No irradiated fuel pins were received from the Westinghouse Advanced Reactor Division (WARD) during the first quarter of FY 1981. Examinations performed on irradiated fuel pins are listed in Table AL-001-IV.

Argonne National Laboratory: One irradiated fuel pin was received from the Argonne National Laboratory during the first quarter of FY 1981. Examinations performed on irradiated fuel pins are listed in Table AL-001-V.

TABLE AL-001-I
POSTIRRADIATION EXAMINATION OF PINS FROM GE

<u>Examination</u>	<u>Pins Examined</u>
1. Density Measurement	4 (12) ^a
2. Longitudinal Grinding and Reimpregnation	2 (2)
3. Transverse Grinding and Reimpregnation	5 (14)
4. Macros and Autoradiography	5 (17)
5. Longitudinal As-Polished Photography	2 (2)
6. Transverse As-Polished Photography	4 (11)
7. Longitudinal Etched Photography	2 (2)
8. Transverse Etched Photography	5 (14)

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

TABLE AL-001-II
POSTIRRADIATION EXAMINATIONS OF PINS FROM HEDL

<u>Examination</u>	<u>Pins Examined</u>
1. Cask Unloading	3
2. Visual Examination	4
3. Preliminary Measurements	4
4. Profilometry Optical	26
5. Radiography, Betatron	17
6. Gamma Scan, Gross	3
7. Gamma Scan, Multispectral	3
8. Gas Sampling and Analysis	2
9. Photography, Full Length, With Wire	2
10. Photography, Full Length, Without Wire	2
11. Photography, Incremental, With Wire	1
12. Photography Incremental, Without Wire	1
13. Wire Wrap Marking	4
14. Wire Wrap Removal	4
15. Sectioning	5
16. Fuel Length Measurement	3
17. Mounting	10 (11)
18. Transverse Grinding and Reimpregnation	6 (6)
19. Sequential Transverse Grinding and Reimpregnation	1 (1)
20. Macros and Autoradiography	6 (7)
21. Transverse As-Polished Photography	6 (7)
22. Transverse Etched Photography	6 (6)

TABLE AL-001-III
POSTIRRADIATION EXAMINATION OF
PINS FROM LOS ALAMOS

<u>Examination</u>	<u>Pins Examined</u>
1. Gas Sampling and Analysis	4
2. Sectioning	4

TABLE AL-001-IV
POSTIRRADIATION EXAMINATION OF PINS FROM WARD

<u>Examination</u>	<u>Pins Examined</u>
1. Visual Examination	4
2. Preliminary Measurements	4
3. Profilometry, Optical	4
4. Gamma Scan, Gross	4
5. Gamma Scan, Multispectral	4
6. Gas Sampling and Analysis	10 (14)
7. Photography, Incremental, Without Wire	1

<u>Examination</u>	(cont'd.)	<u>Pins Examined</u>
8. Sectioning		14
9. Density Measurements		13 (70)
10. Microprobe Analysis		2 (3)
11. Fuel Dissolution		1 (4)
12. Longitudinal Grinding and Reimpregnation		3 (6)
13. Transverse Grinding and Reimpregnation		4 (5)
14. Macros and Autoradiography		3 (11)
15. Longitudinal As-Polished Photography		1 (1)
16. Transverse As-Polished Photography		1 (1)
17. Longitudinal Etched Photography		3 (6)
18. Transverse Etched Photography		4 (5)

TABLE AL-001-V
POSTIRRADIATION EXAMINATIONS OF PINS FROM ANL

<u>Examination</u>	<u>Pins Examined</u>
1. Cask Unloading	1
2. Visual Examination	2 (3)
3. Preliminary Measurements	2 (3)
4. Profilometry, Optical	1
5. Radiography, Betatron	2 (3)
6. Gamma Scan, Gross	2
7. Gamma Scan, Multispectral	2
8. Gas Sampling and Analysis	1 (2)
9. NaK Removal	1
10. Bonding Removal	1
11. Eddy Current Scan	1
12. Sectioning	1
13. Density Measurement	1
14. Microprobe Analysis	1

SHIPMENTS MADE DURING 1ST QUARTER FY 1981

<u>Shipments to:</u>	<u>Material</u>
HEDL	One Irradiated LASL KB Pin
ANL/W	One Irradiated HC4A Pin

V. QUALITY ASSURANCE
(S. N. Dresback)

A. Analytical Chemistry

The documentation for three shipments was reviewed and released to the shipping department.

B. Hot Cell Operations

1. Six procedures were reviewed and approved

for use on applicable quality assurance programs.

2. One shipping document was reviewed and released to the shipping department.
3. Sixteen element examination data packages were overchecked prior to shipment to the experimenter.

C. Microstructure Analysis

A total of sixty-three data packages for samples were overchecked prior to shipment to the experimenters, seven for HEDL, sixteen for WARD and forty for Los Alamos.

VI. PUBLICATIONS AND TALKS

1. S. F. Marsh, M. R. Betts, and J. E. Rein, "Determination of Submicromolar Amounts of Uranium (VI) by Compleximetric Titration with Pyridine-2, 6-Dicarboxylic Acid," Anal. Chim. Acta. 119, 401-404 (1980). (LAUR-80-974).

VII. REFERENCES

1. M. Cannon, Los Alamos National Laboratory unpublished work (1980).
2. T. F. Budinger and G. T. Gulberg, "Three-Dimensional Reconstruction in Nuclear Medicine by Iterative Least-Squares and Fourier Transform Techniques," Lawrence Berkeley Laboratory report LBL-2146 (1974).
3. G. N. Minerbo and G. Sanderson, "Reconstruction of a Source from a Few (2 or 3) Projections," Los Alamos Scientific Laboratory report LA-6747-MS (1977).
4. G. Minerbo, "MENT: A Maximum Entropy Algorithm for Reconstructing a Source from Projection Data," Computer Graphics and Image Processing, 10, 46-48 (1979).
5. G. Frieder and G. T. Herman, "Resolution in Reconstructing Objects from Electron Micrographs," J. Theor. Biol., 33, 189-211 (1971).
6. W. J. Maraman, "Examination of Fast Reactor Fuels and FBR Analytical Quality Assurance Standards and Methods, July 1-September 30, 1979," Los Alamos Scientific Laboratory report LS-8132-PR (1979).
7. S. F. Marsh, M. R. Betts, and J. E. Rein, "Determination of Submicromole Amounts of Uranium by Complexometric Titration with Pyridine-2, 6-Dicarboxylic Acid," Anal. Chim. Acta, 119, 401-404 (1980).
8. L. D. McIsaac, J. D. Baker, J. F. Krupa, R. E. LaPointe, D. H. Meikrantz, and N. C. Schroeder, "Study of Bidendate Compounds for Separation of Actinides from Commercial LWR Reprocessing Wastes," Idaho National Engineering Laboratory report ICP-1180 (1979).

PROJECT AL-003

FBR ANALYTICAL QA STANDARDS

October 1 — December 31, 1980

Person in Charge: W. J. Maraman

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 used to evaluate reactor components relative to specifications. A new task is developing procedures for preparing uranium oxide pellets containing characterized levels of various components for use as quality assurance materials in the Secure Automated Fabrication (SAF) facility being constructed at the Hanford Engineering Development Laboratory (HEDL). A major continuing task is preparation and distribution of calibration and quality control materials for use in FFTF fuel production quality assurance programs.

II. QUALITY ASSURANCE MATERIALS FOR SAF

(G. R. Waterbury and Staff)

Based on a meeting of HEDL and LASL personnel in October, our effort this year is the development of procedures for preparing two types of pellets for use in evaluating analyzers being constructed for the Close-Coupled Analytical (CCA) at-line facility of the SAF. One type is pellets of mixed cerium-uranium oxide prepared to have hypo-stoichiometric O/M ratios when analyzed by a thermogravimetric analyzer. The fuel preparation procedure being evaluated is a HEDL preparation in which blends of CeO_2 and UO_2 are heated sequentially in various atmospheres including a He-H_2 mixture.

The second pellet type is uranium oxide containing homogeneous concentrations of carbon, chloride, fluoride, nitrogen, and sulfur at levels

from low to several hundred parts per million. A low temperature, high-pressure molding of a powder blend of uranium oxide, aluminum metal, and impurity compounds is being investigated. Pellets of the desired dimensions (6.4 mm long by 5.1 mm diameter or 0.25 in. long by 0.20 in. diameter) without added impurity compounds have been prepared for physical testing to establish their fracture resistance.

III. CALIBRATION AND QUALITY CONTROL MATERIALS FOR FFTF FUEL PRODUCTION SURVEILLANCE

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

HEDL has requested three materials, each having a uranium oxide matrix. The first material is a series of six blends containing nonmetal (C, Cl, F, N, P, and S) impurities for use as quality control samples. This material was shipped to HEDL during November. The other two materials, that serve for calibration of analytical methods, consist of a graded concentration series of nonmetals and graded concentration series of 29 metal impurities. Various uranium oxide batches are being analyzed for nonmetal and metal impurities whose concentrations must be low for use as blend matrices.

IV. CHARACTERIZATION OF LOS ALAMOS PRODUCED PLUTONIUM OXIDE

(G. R. Waterbury and Staff)

Los Alamos continued production of the plutonium oxide source material for FTR mixed oxide fuel production. Each produced batch is analyzed for chemical specifications of plutonium assay, plutonium isotopic distribution, ^{241}Am , C, Cl, F, N, P, S, 29 metal impurities, and trace uranium.