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PNL TEST PROCEDURE

TITLE: HTA-3-3, SOLIDS ANALYSIS: X-RAY DIFFRACTION ANALYSIS

1.0 APPLICABILITY

This procedure provides guidelines for x-ray diffraction analysis of solids. The procedure applies to solids analysis conducted for waste repository programs. It also applies to work conducted for other waste repository supporting organizations, such as the Materials Characterization Center (MCC).

This procedure is not limited to a particular type or form of solid. Solid samples for analysis may include metals and nonmetals, organic or inorganic materials, and may be examined as powders, fragments, monoliths, sheets, wires, or any other form of appropriate dimensions.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- X-ray generator.
- X-ray diffractometer.
- X-ray diffraction film cameras.
- Computer-based data acquisition, diffractometer control, and analysis systems.

NOTE: Operation of the above equipment is described in the appropriate manufacturers' operating instructions. These instructions shall be referenced on the x-ray operator's laboratory notebook.

Concurrence NA	Date	Approved J. McCown	Date 7/2/87
Prepared by	Date 1 July 87	QAD Concurrence B.O. BARNES	Date 6/30/87
Procedure No. HTA-3-3	Revision No. 3	Effective Date JUL 01 1987	Page 1 of 5

4.0 PROCEDURE

4.1 Description of Method

For solids analysis, x-ray diffraction analysis is used for crystalline phase identification and crystallographic phase characterization. The geometry and intensity of x-ray diffraction from a material provide a basis for identifying the material and determining its atomic structure. Crystalline phases are identified by matching x-ray peak positions and intensities with standard peak pattern and intensity data. The Joint Committee for Powder Diffraction Standards' (JCPDS) data base is used as the primary source of known x-ray patterns and intensities. X-ray diffractometry (XRD) is a method that allows automated (computer-controlled) data collection and data reduction. Film camera methods (e.g., Debye-Scherrer or Gandolfi camera powder diffraction) are alternatives that may be preferred for analyzing small sample fractions or limited sample quantities. In some systems the function of the film camera is accomplished with solid-state position-sensitive detectors that record x-ray line position and intensity data directly in a computer. In the XRD method, diffracted x-rays are detected electronically as the sample is step-scanned through small-angle increments over a range of angles encompassing the characteristic diffraction lines for most materials. Scanning and x-ray counting are performed under computer control, and the data are stored in the computer system for later analysis. Comparison of experimental data with the JCPDS data resident in the computer system may be made by the computer but must be verified by a human operator. The JCPDS data base is also available on cards and in compiled volumes of card images. For film camera methods of x-ray analysis, the x-ray line position and intensity information is measured by a human operator with various aids, including automatic measuring film densitometers.

4.2 Specimen Preparation

Preparation methods for x-ray diffraction analysis samples depend on the material and type of analysis to be performed. Following are guidelines for preparing the samples most often related to waste repository work for diffractometer and camera analyses. Describe any unusual aspects of sample preparation in a laboratory notebook.

4.2.1 Powder Samples

Reacted solids from hydrothermal tests are generally sampled as wet powders. Powdered materials containing radioactive materials must be prepared in a hood or glovebox designated for such materials. A procedure for preparing powder samples for XRD analysis follows:

Step 1) After air-drying the sample, mix ~10 mg of sample in a 1:4 collodion isoamyl acetate solution.

Step 2) Grind the sample in a boron carbide mortar with a pestle.

Step 3) Spread the ground sample within a designated area of a petrographic slide with a pipette and allow to dry in air for 24 hours. (The collodion serves as a binder.) Cover sample when dry to avoid contamination by other materials.

Step 4) Transfer the mounted sample from the glovebox to a connected hood where the sample is smeared to remove loose contamination from the uncoated slide area.

Step 5) Coat the slide on both sides with a thin layer of Krylon acrylic spray to eliminate smearable contamination. The Krylon spray may be omitted at the discretion of the cognizant scientist. A note should be made on the sample follower card if the spray is not applied.

Step 6) Clean the mortar and pestle used for sample grinding with four methanol washes. (Do this after each use to prevent sample cross-contamination.)

Step 7) Check that sample identification has been maintained throughout the sample preparation and that each petrographic slide mount has been marked with the sample identification number.

Powder samples for Debye-Scherrer camera analysis may be prepared by gluing a small quantity of sample material on the tip of a glass wand or glass capillary with collodion/amylacetate solution or other adhesives. Mount the wand or capillary sample into the x-ray camera and align the sample so that it moves eucentrically in the x-ray beam path. Individual particles for analysis with a Gandolfi precession holder in the Debye-Scherrer camera can also be prepared by this method.

4.2.2 Massive Samples

Massive samples for XRD analysis should present a clean, polished, flat surface to the x-ray beam in the diffractometer and be of suitable dimensions to be mounted in the diffractometer sample holder. The specific preparation procedure will be documented in the x-ray sample laboratory notebook.

4.2.3 Nonroutine Samples

Samples that require special preparation because of the nature of the sample or the analytical request shall be noted in the x-ray sample laboratory notebook. Nonroutine procedures shall be recorded in the notebook.

4.3 XRD Calibration

Calibration of equipment shall be in accordance with PAP-1201.

X-ray diffractometers shall be calibrated with a certified alpha-quartz standard at least semiannually. Additional calibration may be performed by the cognizant scientist. The calibration record will include a plot of the error in diffraction angle versus the diffraction angle. If the error in diffraction angle at the quartz 100% relative intensity peak exceeds ±0.06 degrees, instrument realignment will be required. This may be performed by a manufacturer's field service engineer.

4.4 Data Analysis

Operation of the XRD system is performed under computer control, using run parameters set up at the beginning of the run. This allows the operation from data acquisition to automated peak search and data reduction to proceed without operator intervention. The output of a computer analysis will include a record of the run parameters, a listing of all x-ray peaks identified, diffractogram plots of intensity versus diffraction angle and results of any automated search/match analysis with JCPDS data. Raw diffraction data shall be recorded by the computer for permanent storage. Analysis output shall include sample identification code as indicated by the sample follower card and shall be cross-referenced in the x-ray operator's laboratory notebook.

X-ray camera analyses may be performed from x-ray peak position and intensity data measured from film or recorded from a position-sensitive x-ray detector. Once the data are entered into a computer, analysis can proceed by the same method used for x-ray analysis. Measurements from camera film shall be recorded in a x-ray camera analysis notebook.

4.5 Sample Identification

Sample identity shall be maintained at all times during preparation, transportation, analysis, and storage, in accordance with PAP-801. Samples shall be identified by codes marked on sample containers and holders. Prepared samples shall be kept in storage for at least one year. Disposition of archived samples is covered in HTA-1-1.

4.6 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks provide a mechanism for control of most records.

The following records of x-ray diffraction analyses shall be maintained:

- X-ray sample preparation laboratory notebook

- X-ray operator's laboratory notebook
- X-ray analysis output including run parameters and peak listings
- Spectra stored on magnetic media with backup copies per PAP-1701
- X-ray camera analysis notebook.

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August 4, 1989

Dr. Ray Stout, L-201
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA 94550

Dear Ray:

Attached is a revised copy of the "Addendum to Test Plan for Long-Term, Low-Temperature Oxidation of High Burnup Spent Fuel."

If you have any questions, please contact me on FTS 444-3453.

Sincerely,

Dr. Robert E. Einziger, Manager
Materials & Chemical Systems Performance Section

REE:neb
Attachment

cc: SC Marschman - PNL

Addendum to Test Plan for Long-Term, Low-Temperature Oxidation of High Burnup Spent Fuel

R. E. Einziger

January 1989

1.0 INTRODUCTION

The Yucca Mountain Project Office (YMPO) is evaluating a site at Yucca Mountain, Nevada, to determine the suitability of this site for a high-level nuclear waste repository. The horizon that is under investigation for repository development is the Topapah Spring Member of the Paintbrush Tuff, a welded, devitrified ash flow tuff. At Yucca Mountain, this unit lies in the unsaturated zone; the water table is hundreds of meters below the reference repository horizon. Lawrence Livermore National Laboratory (LLNL) is developing designs for waste packages and testing the performance of waste forms and metal barriers under expected repository conditions for the YMPO Project.

The Environmental Protection Agency (EPA) (40 CFR 191 1982) and the Nuclear Regulatory Commission (NRC) (10 CFR 60 1983) have imposed requirements limiting potential radionuclide release from a high-level nuclear waste repository. The potential change in the oxidation state of spent fuel during its residence in a repository must be known to evaluate radionuclide retention capabilities of the repository. Analyses indicate that UO_2 will oxidize to higher states under the temperature and atmospheric conditions expected in a tuff repository (Einziger and Woodley 1985). If oxidation progresses sufficiently, cladding that contained breaches might split open, or significant quantities of higher oxides with potentially higher leach rates might form.

An integrated technical approach (Einziger 1985) was developed to study spent fuel oxidation at low temperatures characteristic of the post-container breach period. The objective of the long-term oxidation testing is to verify at low temperatures the predictions based on the thermogravimetric analysis (TGA) results of the influence of important fuel characteristics (i.e., gas release, burnup, fuel type, etc.) and atmospheric variables (i.e., moisture content, radiation field) on oxidation rates and mechanisms. Series 1 tests were designed to verify the effects of atmospheric moisture, temperature, and particle size on the oxidation rate and phase formation in pressurized-water reactor (PWR) fuel. Series 2 tests had the same goals as Series 1 except that boiling-water reactor (BWR) spent fuel was used. These tests will also provide fuel at various stages of oxidation for comparative dissolution tests with as-irradiated fuel. Both of these series had detailed test plans (Einziger 1986 and 1987). This test plan addendum to the Series 2 Test Plan is for Series 3, and will present the details for the long-term, low-temperature oxidation tests of high burnup PWR spent fuel that has high and low gas release.

2.0 ADDENDUM

Series 3 will use the same equipment, test temperatures, fuel particulate sizes, atmospheres, radiation fields, sample preparation, sample identification, pre-test characterization, test operation, post-test evaluation, analyses of data, procedures, reporting, data recording, and quality assurance as Series 2. The reader is referred to the Series 2 test plan (Einziger 1987) for a detailed description of these items. The main differences in the Series 2 and Series 3 tests are the type of fuel being tested and number of samples in the test matrix.

2.1 Fuel Characteristics

Series 3 will use high burnup fuel with high and low gas releases. High burnup PWR fuels manufactured by Combustion Engineering and irradiated in the Calvert Cliffs Unit reactor were acquired by the Materials Characterization Center (MCC) for use as ATM-104 and ATM-106. The fuel characteristics are given in Table 2.2. ATM-104 is thought to represent a high burnup, low fission gas release PWR fuel. ATM-106 is thought to represent a high burnup, high fission gas release BWR fuel.

TABLE 2.1 Characteristics of High Burnup Calvert Cliffs PWR Fuel From Combustion Engineering

Fuel Type	ATM-IC4	ATM-106
Assembly Identification	D047	BT03
Discharge Date	April 17, 1982	October 18, 1980
Nominal Burnup	~43GWd/MTU	~43 MWd/kgM
Fission Gas Release	1.1%	18%
Initial Enrichment	3.038%	2.453%
Initial Pellet Density	94-96% TD	92-24% TD
Initial Rod Diameter	1.118 cm	1.118 cm
Cladding Material	Zircaloy-4	Zircaloy-4
Cladding Thickness	0.066 cm	0.066 cm
Rod Identification	MKP-701	NBD131
Sample Location	*	*

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* Location of samples is as yet undetermined, the location will be recorded in the laboratory record book (LRB).

The MCC has characterized the rods (Guenther 1988 and 1987). Prior to cutting, the rods were punctured for both chemical and isotopic fission gas sampling. Gross and spectral gamma scanning were used to determine the burnup profile. Burnup analyses was conducted at three locations in the bottom half of the rod. Transverse and longitudinal ceramography examinations were performed adjacent to the burnup samples to determine grain size and to look for unusual features.

2.2 Test Matrix

The initial test matrix for the Series 3 tests, consisting of two sets of 27 samples each, is given in Table 2.2. The matrix in Table 2.2 will be repeated for the ATM-104 and ATM-106 fuel. The justification for the choice of variables that follows is given either in the Series 2 test plan (Einziger 1987) or below. The matrix may be adjusted to reflect the latest data from ongoing tests and data obtained as the test progresses.

TABLE 2.2 Test Matrices for Series 3 (High Burnup Fuel) Dry Bath Oxidation Tests

Temperature, °C	Atmospheric Moisture Levels, dew point°C	Number of Samples(a) of Size Indicated(d)			Test Duration
		Fragments	-10/+24 Mesh	-24/+60 Mesh	yr (no.of samples)
175	80	2			2 (2)
	-55	5	1	1	(b), (c)
130	80		2		2 (2)
	-55	1	5	1	(b), (c)
110	80			2	2 (2)
	-55	1	1	5	(b), (c)

(a) Each Sample weighs ~10g
(b) Single samples will go the full 2 yr.
(c) Three of the multiple samples will go the full 2 yr; others will be removed for between 6,000 and 12,000 h for examination.
(d) Maximum diameter of particle passing through each Tyler screen is: 10 mesh = 1.7 mm, 24 mesh = 0.71 mm, 60 mesh = 0.25 mm.

2.3 Number of Samples and Test Duration

Tests under each set of temperature and atmospheric conditions will start with either two or seven samples containing fragments or pulverized fuel of different size fractions (see Test Matrix - Table 2.2). The mix of sample sizes was guided by the size fractions used in the sister drybath oxidation tests. The predominant sample type at each temperature is the smallest size fraction that is expected to yield substantial weight gains. The purpose of including a single sample of each of the remaining two size fractions is to confirm at lower temperature the particle size effects seen in the PWR fuel oxidation tests (Einziger and Buchanan 1987). No moisture effects are expected, so only two samples will be included in the high-moisture baths. These samples will be used for comparison with the five samples in the -55°C dew point atmosphere.

Including shutdown and startup time, each complete interim examination will require 5 days. To maximize the time-at-temperature, interim examinations will be conducted approximately every 6 weeks to 2 months. This frequency of examination has worked satisfactorily with the other tests.

According to the test matrix (Table 2.2), either one, three, or five samples of any particular type (i.e., fragments, -10/+24 mesh, or -24/+60 mesh) will be run in a test. If five samples are used, two samples will be removed between 6,000 and 12,000 h. The three remaining samples will be tested for the duration, currently estimated to be 2 years. If two samples are used, both will remain for the duration of the test. If a single sample is used, it will remain for the full test duration. Additional samples may be placed under test, replacing those removed, if such action is indicated to be necessary by fuel examinations. The intervals for fuel sample removal may change as a result of the ceramographic, electro-optical, and leaching examinations.

3.0 REFERENCES

40 CFR 191, Dec. 29, 1982. Environmental Protection Agency, Proposed Rule, Vol. 47, No. 250.

10 CFR 60, June 30, 1983. "Disposal of High-Level Radioactive Wastes in Geologic Repositories--Licensing Procedures," Title 10, Chapter 1, Part 60.

Einziger, R. E. and R. E. Woodley. 1985. Evaluation of the Potential for Spent Fuel Oxidation Under Tuff Repository Conditions. HEDL-7452, Hanford Engineering Development Laboratory, Richland, Washington.

Einziger, R. E., 1985. Technical Test Description of Activities to Determine the Potential for Spent Fuel Oxidation in a Tuff Repository. HEDL-7540, Hanford Engineering Development Laboratory, Richland, Washington.

Einziger, R. E., 1986. Test Plan for Long-Term Low-Temperature Oxidation of Spent Fuel-Series 1. HEDL-7560, June.

Einziger, R. E., 1987. Test Plan for Long-Term, Low-Temperature Oxidation of BWR Spent Fuel. Pacific Northwest Laboratory

Guenther, R. J., D. E. Blahnik, T. K. Campbell, V. P. Jenquin, J. E. Mendel, and C. K. Thornhill, 1988. Characterization of Spent Fuel Approved Testing Material--ATM-106. PNL-5109-106, October.

Guenther, R. J., D. E. Blahnik, T. K. Campbell, U. P. Jenquin, J. E. Mendel, and C. K. Thornhill, 1987. Characterization of Spent Fuel Approved Testing Material--ATM-104. September.

Einziger, R. E. and H. C. Buchanan, 1987. Interim Transition Report, Long-Term Low-Temperature Oxidation of PWR Spent Fuel. WHC-EP-007, Westinghouse Hanford Company, Richland, Washington.

Appendix D - Estimated Staffing Requirements for Series 3 Oven Oxidation Tests*.

	FTE
Scientist (PNL)	.56
Secretarial (PNL)	.05
Technicians (PNL)	.08
Program Manager (PNL)	.42
Task Leader (LLNL)	.10
Total FTE	1.21

* These estimates are based on currently planned Series 3 oven oxidation tests described in Appendix C.