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R. E. Einziger

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Prepared for
Lawrence Livermore National Laboratory
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with the U.S. Department of Energy
Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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SUMMARY

Preliminary studies indicated the need for more spent fuel oxidation data in order to determine the probable behavior of spent fuel in a tuff repository. Long-term, low-temperature testing was recommended in a comprehensive technical approach to 1) confirm the findings of the short-term thermogravimetric analysis tests; 2) evaluate the effects of variables such as burnup, atmospheric moisture, and fuel type on the oxidation rate; and 3) extend the oxidation data base to representative repository temperatures and better define the temperature dependence of the operative oxidation mechanisms.

This document presents the test plan to study the effects of atmospheric moisture and temperature on oxidation rate and phase formation using a large number of boiling-water reactor fuel samples. Tests will run for up to two years, use characterized fragmented and pulverized fuel samples, cover a temperature range of 110°C to 175°C, and be conducted with an atmospheric moisture content ranging from <-55°C to ~80°C dew point. After testing, the samples will be examined and made available for leaching testing.

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1.0 INTRODUCTION

The Yucca Mountain Project Office (YMPO) is evaluating a site at Yucca Mountain, Nevada, for the U.S. Department of Energy (DOE) Office of Civilian Radioactive Waste Management (OCRWM) 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 Topopah 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)(1) and the Nuclear Regulatory Commission (NRC)(2) 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 its radionuclide retention capabilities. Analyses(3) indicate that UO_2 will oxidize to higher states under the temperature and atmospheric conditions expected in a tuff repository. If the oxidation progresses sufficiently, cladding that contained breaches might split open, or significant quantities of higher oxides with potentially higher leach rates might form.

1.1 OBJECTIVE OF DRY BATH TESTING

An integrated technical approach(4) was developed at Pacific Northwest Laboratory(a) 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

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(a) Operated for U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

mechanisms. In particular, the 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. These tests will also provide fuel at various stages of oxidation for comparative leaching tests with as-irradiated fuel. This plan will present the details for the long-term, low-temperature oxidation tests of moderate burnup boiling-water reactor (BWR) spent fuel.

1.2 BACKGROUND

The spent fuel oxidation data base was extensively reviewed prior to the start of the Series 1 PWR tests. A complete data evaluation, found in Reference 3, is summarized below. Based on the anticipated and possible atmospheres the rods might experience, several shortcomings in the data base were identified. Most UO_2 oxidation data are gathered above 200°C and then extrapolated to lower temperatures. The data indicate little or nothing about the rate of formation of intermediate oxides, or which oxides are formed; the data usually relate to the time period before spallation resulting from the formation of U_3O_8. Assuming conservatively that the container breaches between 300 and 1000 years, the fuel temperature will be between 160°C and 110°C. There are relatively few data to indicate how rapidly U_4O_9 and U_3O_7 will form at temperatures between 160°C and 110°C. A time-dependent extrapolation(4) of the high-temperature data (5) indicates that insufficient fuel will oxidize to U_3O_8 in 3000 years to cause disruption of the cladding. This extrapolation is predicated on the assumption that there are no additional low activation energy or thermal fuel oxidation mechanisms taking place that are insignificant at the higher test temperatures but become dominant at the lower repository disposal temperatures. These extrapolations are based on oxidation data from PWR fuel using laboratory air with normal moisture content. The effect of the moisture content of the air and the validity of using PWR fuel oxidation data for BWR rod performance predictions are unknown.

Recent oxidation studies have been done in Canada and the U.S.A. at temperatures below 200°C with a range of moisture in the atmosphere. Canadian deuterium uranium (CANDU) fuel, which has a high linear heat rating, showed a strong enhancement of grain boundary attack with a saturated moist atmosphere at 150°C.(6) The majority of the oxidation work has been conducted on PWR fuel. The few studies on BWR fuel looked at burnup effects and powder formation.(7) Burnup over the range of 10 to 35 GWd/MTU had little effect on the oxidation rate of Quad Cities BWR fuel at 230°C. Monticello experimental BWR rodlets showed as much as 2% weight gain, equivalent to that of U_3O_7, in only 6000 h at 170°C; however, the uncertainty was as much as 50%. The efforts of that BWR study and its companion PWR studies(7) were aimed more at determining powder formation applicable to dry storage than mechanisms of U_3O_7 formation applicable to repository work. Little difference was found between the behavior of BWR and PWR fuel. These BWR and PWR studies were conducted in a strong (5×10^5 R/h) imposed gamma field, which would not be present in the repository but which might affect the laboratory results.

Fifty PWR fuel samples are being oxidized in air with dew points of ~+80°C and -74°C at 175°C, 130°C, and 110°C. Though the tests have run for only 3200 to 5800 h, some preliminary observations can be made.(8)

1. At temperatures above 175°C, the rate of weight gain due to oxidation is independent of the particle size, but at lower temperatures the rate is dependent on the particle size. The largest particles oxidize slowest.
2. Over the dew point range of -74°C to 80°C, the moisture in the air appears to have no effect on the oxidation rate.
3. When multiple identical samples are oxidized, there is scatter in the oxidation data of ~20%. This must be accounted for when making extrapolations or performing temperature change oxidation studies using only a few samples.

It is expected that the testing of BWR fuel proposed in this test plan will yield similar results.

2.0 TEST DESCRIPTION

The tests described in this plan will be conducted in a bank of six covered dry baths that provide the proper atmosphere. The fuel samples will come from Cooper BWR fuel rods. After the test, samples may be examined by x-ray diffraction (XRD), ceramography, transmission electron microscopy (TEM)/electron diffraction, or other means before being made available for leaching experiments. The data will be compared with predictions based on the TGA testing of(9) BWR fuel and dry bath oxidation of PWR fuel(8) to confirm the oxidation mechanisms and compare behavior. These tests, which will run for up to two years, will be used to confirm the effects of atmospheric moisture and temperature.

2.1 TEST MATRIX

The initial test matrix for the Series 2 tests, consisting of 30 samples, is given in Table 2.1. The justification for the choice of variables that follows is based primarily on the PWR fuel testing series.(8) The matrix may be adjusted to reflect the latest data from the TGA testing program(9) and data obtained as the test progresses.

2.1.1. Test Temperature

Tests will be conducted at 175°C, 130°C, and 110°C. A major function of the testing is to define the rate constant (k') versus 1/T curve. Since the intermediate temperature data are being gathered on the TGA apparatus(9) and the low-temperature data in the present dry bath tests, one set of the dry bath tests will be run at 175°C to provide temperature range overlap between the two sets of tests.

Test temperatures of 130°C and 110°C were chosen for the PWR Series 1 tests to extend the rate constant curve to the lowest possible experimental temperature that is expected to produce measurable oxidation in a 2-year test. The Series 1 Test(10) plan describing the dry bath testing of PWR fuel provides the rationale for temperature selection. The selection of these temperatures was dictated by 1) an expected weight gain of the crucible of ~2 mg

TABLE 2.1. Test Matrix BWR Dry Bath Oxidation Tests

Temperature, °C	Atmospheric Moisture Levels, dew point °C	Number of Samples[a] of Size Indicated[d]			Test Duration, yr (no. of samples)
		Fragments	-10/+24 Mesh	-24/+60 Mesh	
175	80	3			2 (2) 1 (1)
	-55	5	1	1	(b), (c)
130	80		3		2 (2) 1 (1)
	-55	1	5	1	(b), (c)
110	80			3	2 (2) 1 (1)
	-55	1	1	5	(b), (c)

(a) Each sample weighs ~10 g.
(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.

after 2 years and 2) the prediction of a measurable sample weight gain based on the TGA data. However, the measured weight gain of the crucibles has been at most 0.2 mg, an order of magnitude less than expected. In addition, the measured weight gains of the samples have not been as large as expected.

In spite of the uncertainties in the extrapolations there have been sufficient weight gains at 110°C to make meaningful and reproducible measurements on the PWR fuel. Because there was no reason to choose a different temperature, and in order to place the BWR samples in the same dry baths with the PWR samples, a lower test temperature of 110°C was again chosen. Similarly, the intermediate temperature is the same as for the PWR spent fuel tests, 130°C. This temperature was chosen to split the reciprocal temperature range between 175°C and 110°C.

2.1.2. Fuel Particle Size

During irradiation, spent fuel typically cracks into fragments with an average equivalent spherical diameter of ~0.4 cm. Since air can readily penetrate the relatively large cracks between fragments, an oxidation sample consisting of a number of fragments would represent the expected condition of the fuel in the repository. Earlier testing(11) indicated that oxidation may be a two-step process consisting of oxygen diffusion down the grain boundary, followed by diffusion of oxygen into the grains; the second step is the rate-controlling mechanism. If the grain boundary diffusion is rapid with respect to the test duration, such as in the tests at 200°C and 225°C, then samples consisting of fragments are suitable as test specimens.

If diffusion down the grain boundaries takes longer than the test duration, then measuring weight gain of fuel fragments will not reflect the rate-limiting diffusion into the grains.(12) The grain boundary diffusion step can be significantly enhanced if the fragments are pulverized into smaller particles.

Thermogravimetric analysis testing of PWR fuel(13) indicated that pulverization does little to enhance oxidation above 175°C. At 140°C there appeared to be some enhancement of the oxidation. This observation was supported by the results of the dry bath oxidation tests on PWR fuel,(8) which showed no enhancement at 175°C but a distinct spread of over a factor of 2 in the rate of weight gain due to oxidation for the different particle sizes at 130°C and 110°C. A lengthy argument based on the onset of bulk diffusion was made in the Series 1 test plan(10) to justify the selection of particle size. The reasoning presented there still holds. The particle sizing for the pulverized fuel used in the Series 1 PWR fuel oxidation tests will again be used in the BWR fuel oxidation tests.

Fuel can easily be sieved or pulverized so that each size fraction has the same chemical composition and radiation spectrum. In the 175°C experiment, as-irradiated fragments will be used primarily. Pulverized samples, primarily in the -10/+24 Tyler mesh range, will be used in the 130°C test, and pulverized samples, primarily in the -24/+60 Tyler mesh range, will be used in the 110°C test. The maximum diameter of particles passing through the number 10, 24, and 60 Tyler meshes are 1.7 mm, 0.71 mm, and 0.25 mm, respectively. The complete matrix is in Table 2.1.

2.1.3. Moisture in the Atmosphere

In a tuff repository the spent fuel is expected to be in a water-saturated air atmosphere with a dew point near 95°C. Thermogravimetric analysis tests on PWR fuel(13) indicated that a variation in the dew point of air between 14.5°C and -70°C has little or no effect on the oxidation rate of spent fuel. Similarly, moisture up to a dew point of +80°C was found to have no effect in the Series 1 dry bath oxidation tests of PWR spent fuel.(8) Three of the nine dry bath systems have been designed to accommodate an atmosphere with a moisture content up to a dew point of 80°C by heating all the associated gas lines. To extend the TGA results based on PWR fuel to moisture levels nearer those expected in the repository for BWR fuel, tests will be conducted at dew points of ~80°C (~400,000 ppm) and <-55°C. If a moisture dependence is observed, then the test matrix will be amended to include test samples in an atmosphere with a dew point between +10°C and -30°C.

2.1.4. Number of Samples and Test Duration

Tests under each set of temperature and atmospheric conditions will start with either three or seven samples containing fragments or pulverized fuel of different size fractions (see Test Matrix - Table 2.1). The mix of sample sizes was guided by the size fractions used in the sister PWR fuel test. 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.(8) No moisture effects are expected, so only three samples (enough to test reproducibility) 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 takes approximately 3 days. When combined with the time required to examine the PWR samples now under test, the examination time will increase to 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 PWR fuel samples. If the weighing can be conducted while some of the baths remain at temperature without affecting either the accuracy of the balance or the temperature stability of those baths still operating, interim examinations may be conducted more frequently.

According to the test matrix (Table 2.1), 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 three samples are used, one will be removed at ~1 year and two 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.

2.1.5. Radiation Fields

No external radiation fields will be applied to the samples because the fields expected at the time of container breach are nearly the same or less than the self fields generated by samples of ten-year-old fuel used in these tests. Therefore, the results should establish a conservative upper bound with respect to radiation enhancement of oxidation at repository conditions.

The alpha field resulting from the decay of the actinides, which can cause localized ionization of the oxygen, will be predominant after 1,000 years. Since the actinides responsible for the alpha activity do not readily migrate, and the actinides have very long half-lives, the alpha fields at 1,000 years and at emplacement will not differ significantly. Since the alpha is a short-range particle, the radiation field resulting from alpha decay is independent of sample size when the sample is over ~30 μm in diameter.

The neutron field present in the reactor is far greater than that ever experienced by the fuel in the repository. All the atomic displacement damage that might significantly affect the oxidation rate of the fuel will have occurred in the reactor. No further neutron radiation damage is expected in the repository.

The gamma field at the external surface of the container that is due to fission products will have dropped from ~6 x 10^4 R/h at the time of emplacement to ~70 R/h after 300 years. By 1000 years after emplacement, the gamma field will have dropped to ~4 R/h. Since UO_2 is such an efficient gamma shield, over 80% of the radiation experienced by the fuel is supplied by its first and second nearest neighbors in a close-packed array. In a test sample, this self field, depending on whether the fuel is fragmented or pulverized, ranges from 0.1 to 0.05 of the gamma field that the fuel would have experienced had it remained in close-packed fuel.(14) On the other hand, the gamma field in ten-year-old fuel is 300 to 12,000 times greater than in 300- to 1000-year-old fuel.(15) Combining the greater field in the fresher fuel with smaller test sample size indicates that even the pulverized ten-year-old fuel has a self gamma field that is over 15 times greater than that emitted by fuel in a consolidated bundle after 300 years. The possibility exists that the higher gamma fields associated with the young fuel used in these tests may produce a higher oxidation rate than would be present at 1000 years in the repository.

2.2 SAMPLE SELECTION, PREPARATION, AND IDENTIFICATION

Boiling-water reactor fuel manufactured by General Electric and irradiated in the Cooper reactor as assembly CZ-346 was acquired by the Materials Characterization Center (MCC) for use as ATM-105. Currently publishable characteristics of the assembly are given in Table 2.2. It is thought to represent an average burnup, low fission gas release BWR fuel. Samples for the TGA tests and companion long-term dry bath tests will come from rod ADD-2974 in position 3C. The history of these rods will be reported by the MCC in early CY 1988. The ATM-105 fuel assembly contains four types of fuel rods: 1) 2.93% U-235 enrichment, 2) 1.94% U-235 enrichment, 3) 1.94% U-235 enrichment plus 4 wt% Gd_2O_3 and 4) 2.93% U-235 enrichment plus 3 wt% Gd_2O_3. The rod that will be used for these oxidation tests is of the first type; i.e., 2.93% enriched uranium with no gadolinium.

TABLE 2.2. Characteristics of ATM-105 Cooper BWR Fuel from General Electric

Fuel Type	BWR 7 x 7
Assembly Identification	CZ-346
Discharge Date	(a)
Nominal Burnup	~26 MWd/kgHM
Fission Gas Release	(b)
Initial Enrichment	2.93%
Initial Pellet Density	(a)
Initial Rod Diameter	(a)
Cladding Material	Zircaloy-2
Cladding Thickness	(a)
Rod Identification	ADD-2974

(a) Information to be provided in a characterization report to be released at a later date by MCC.
(b) To be measured by MCC.

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

These tests are not concerned with burnup effects, so 18 in. of fuel with nearly equal burnup as indicated by the gamma scans will be used for testing. At ~10 g per sample and 31 g of fuel per in., there is sufficient fuel for ~55 samples. The fuel segments will be cut dry into 4- to 6-in.-long pieces for handling purposes. The cladding will be split with a carbide end mill and then pried open for removal of the fuel fragments. Six fragments will be set aside for possible characterization, ~25 fragments will be used in TGA testing, and the remainder of fuel will be used for dry bath test samples.

Each sample consisting of fragments will weigh ~10 grams. The samples are arbitrarily weighed without attempt to individually select fragments. After the samples are separated, they will each be spread in a petri dish and photographed to provide a record of the number of fragments and information for geometric surface area calculations. The samples will then be placed in weighed crucibles and reweighed to obtain the initial weight of the sample.

The fuel to produce specific size fractions will be pulverized in a diamonite mortar. The pulverized fuel will be divided into two groups:(a) -10/+24 mesh and -24/+60 mesh. Approximately 50 mg of each fraction will be set aside for characterization. The remaining pulverized fuel will be divided into ~10-g samples and placed in the preweighed crucibles for initial weight determination.

Three of the fragments for characterization will be taken from a position adjacent to the cladding. A partially cylindrical surface will indicate that position. The remaining three fragments will be from the interior of a pellet. Two fragments of each type may be examined ceramographically to determine grain size and porosity. One fragment of each type may be examined in the scanning electron microscope (SEM) to determine fracture morphology. The extent of the ceramography on the fragments will depend on the quality of the MCC ceramographic examination.

X-ray diffraction will be conducted on only one sample, further pulverized to -250 mesh, because the fuel must be finely ground in order to obtain suitable diffraction patterns. Fuel from each of the pulverized fractions will be examined ceramographically to determine particle size distribution and extent of particle fracturing. The ratio of mobile ^{137}Cs to stationary ^{154}Eu will be measured by gamma spectroscopy to ensure that there has been no chemical fractionation or preferential segregation of grain boundary material caused by the crushing and sieving operations.

Individual samples will be identified at the time the fuel is divided into approximately 10-g batches. For this series, samples will be identified by BWR1-Bu (f, P1, P2)-N where f = fragments, P1 = -10/+24 mesh, P2 = -24/+60

(a) Tyler screen scale equivalent.

mesh, and N is the sample number. For subsequent sample divisions, a suffix (a, b, etc.) will be attached to the sample identification. Bu refers to the burnup of the sample relative to the rod maximum; it will range from zero to one. BWR1 identifies the source of the fuel, which may change in future tests; it corresponds in this case to Cooper fuel.

Methods of physically attaching identification to the sample and crucibles and performing the indicated fuel preparation and characterization will be detailed in approved test procedures.

2.3 EQUIPMENT DESCRIPTION

The test apparatus is essentially identical to that used for the PWR dry bath oxidation tests.(8) It consists of a dry bath, air delivery system, temperature measurement system and sample crucible. There are nine such systems installed in the 327 Building "I" air cell. Adjacent to the cell is a Mettler balance with a sensitivity of ±0.1 mg that will be used to weigh the samples.

The temperature measurement and control system is the same as described in the PWR dry bath oxidation test plan(10) with the following change. Originally, the three thermocouples, one in each of the aluminum blocks of the dry bath, were averaged to determine the operating temperature versus time history for that dry bath. Since the temperature variation between the three thermocouples is 1°C or less in Dry Baths 8 and 3, an average temperature is used for these baths. On the other hand, Thermocouples 6C, 4A, 7C and 2A, in Baths 6, 4, 7, and 2, respectively, indicate temperatures that are ~3°C lower than their counterparts. Due to the configuration in the hot cell, it was not possible to determine if the low temperature reading was due to a slight misalignment of the thermocouple in a block where the actual temperature was the same as the other blocks in the bath, or if the block itself was at a slightly lower temperature due to misalignment on the heating element. Analysis(8) of the temperature data from the PWR fuel oxidation tests Series 1 supports the position that the temperature readings of the thermocouples are real. For these four baths, both an average and block-specific temperatures will be determined. It is expected that an individual sample will be at a uniform temperature known to at least ±3°C, but in reality much nearer ±1°C.

2.4 TEST OPERATION

The test consists of initial startup, interim examinations, and final examinations. This section describes how each activity will be conducted.

2.4.1 Initial Startup

The fuel samples will be poured into the preweighed and numbered crucibles using a stainless steel funnel. The sample number and crucible number will be recorded. The crucible will then be transferred to the weighing bubble adjacent to "I" cell, and the transfer door will be closed to prevent convection drafts. Before weighing each loaded crucible, a 10-g standard traceable to the National Bureau of Standards (NBS) will be weighed. The crucible will be hung from the balance and weighed to ±0.0001 g. The crucible will be removed from the balance, a zero point will be measured, and the crucible will be replaced and reweighed at least six times. Then the 10-g standard will be reweighed. If there is a difference in the standard weight of more than ±0.2 mg, the process will be repeated. After weighing, the crucible will be returned to "I" cell and loaded into a designated location in the dry bath. The location will be recorded on a loading diagram and a protector put over the slot. The process will continue until the bath is loaded as required. In addition, a blank (unfilled) weighed crucible will be in slot B5 of each dry bath. The dry bath lid will be replaced. After the dry bath is brought to temperature, the air flow (moist or dry) will be turned on. In the case of the moist air flow, this order prevents condensation in the dry bath. The test time begins when the test temperature is reached. No correction is made for heatup or cooldown time, which is very short in comparison to the duration of the tests.

2.4.2 Interim Examination

At designated intervals (~6 to 10 weeks) throughout the test, samples will be reweighed. The air flow will be stopped prior to cooling to prevent condensation of any moisture. After the system is cooled, the crucibles will be removed from the dry bath and weighed in the same manner as they were before the test. To maintain sample traceability, at no time will more than one sample be out of the dry bath. The system will be restarted as initially described.

2.4.3 Final Examination

At designated intervals, selected samples will be removed from the tests for interim examinations, for further examination, and for use as leaching samples. After weighing, the fuel will be poured into a labeled metal can for transfer out of the cell. The empty crucible will be ultrasonically rinsed with ethyl alcohol and reweighed.

2.5 POST-TEST SAMPLE EVALUATION

The weight change of the samples will be checked at intervals during the test, but weight measurements cannot determine the uniformity of oxidation or the location of the oxidation process in the sample. Only limited information can be determined about the oxide phases. For instance, complete conversion of UO_2 to U_3O_7 yields a weight gain of 1.98%, and complete conversion to U_3O_8 yields a weight gain of 3.96%. If the sample weight gain is found to be greater than 1.98%, it might be expected that at least some U_3O_8 has formed. However, the sample could be almost uniformly U_3O_7 with a minor amount of U_3O_8, or it could be partly UO_2 and partly U_3O_8. In all likelihood, a combination of the phases will occur. Following the test, selected samples will be examined ceramographically by SEM, XRD and TEM/electron diffraction to obtain additional phase information. All samples consisting of fragments will be visually examined to see if there is any spallation.

The goal of the waste form testing program is to determine the radionuclide release characteristics of the spent fuel waste form. Part of this task is to determine the change in leaching characteristics with oxidation state. After post-test evaluations, the test material will be stored in sealed containers and labeled with the sample identification. These samples will be available for leach testing.

2.5.1. Ceramography

Ceramography will be used to visually determine the gross grain boundary degradation and to evaluate the extent of the oxidation into the fragment from the external surfaces. In addition, it will serve as a sampling guide for taking TEM specimens.

Usually, as-polished ceramography of irradiated fuel reveals very little grain structure. The as-polished ceramographs of the oxidized PWR fuel from the TGA tests(13) were quite different, as shown in Figure 2.1. The grain boundaries are quite noticeable and widened, and within the grains there are rings of various thicknesses that parallel many of the grain boundaries. These rings correlate quite well with the TEM examination and appear to be oxygen rich U_4O_9. The as-polished ceramography of the BWR fuel will be examined closely for both of these features.

2.5.2. X-ray Diffraction (XRD)

X-ray diffraction can be used to determine semiquantitatively the relative amounts of the various phases that are present. The oxide state is determined by comparing the diffraction pattern against standard patterns. Unfortunately, the diffraction patterns of certain oxides such as U_3O_7 and U_4O_9 are similar and difficult to separate, thus complicating interpretation of the patterns. Usually a standard, such as Ag, that has diffraction lines that do not overlap with those of the various uranium oxides, is included in the sample as an internal standard. X-ray diffractometers sample an area that is much greater than one grain, so no information can be obtained on the oxide distribution. Careful x-ray diffraction analysis is vital if accurate estimates of the relative amounts of the various oxides are to be obtained, especially when the weight gain is less than 2%. In the preferred method of XRD, fuel is ground for sample preparation.

2.5.3. Scanning Electron Microscopy (SEM)

Light-water reactor fuel tends to fracture intragranularly, while spallation of the higher oxides tends to occur intergranularly. The fragment surface will be examined for signs of spallation using SEM.

2.5.4. Transmission Electron Microscopy (TEM) and Electron Diffraction

The TEM characterizes the oxidation microstructure on nearly an atomic scale. It reveals local microstructure, chemistry, and crystallography of higher oxide phases that form as oxidation proceeds. It also provides information on the chemical nature and distribution of fission products in the fuel.

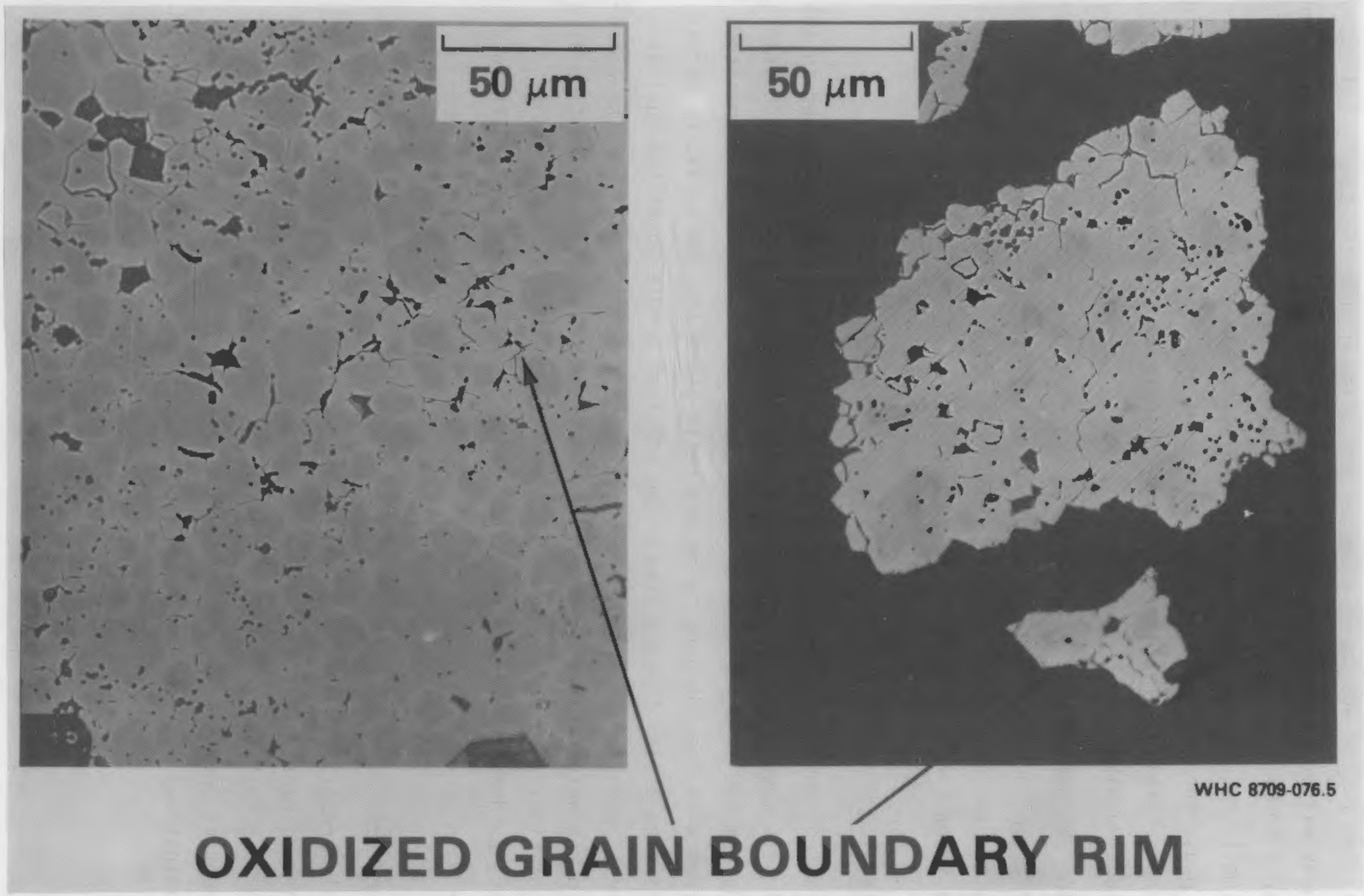

FIGURE 2.1. As-Polished Ceramography of Oxidized Fuel Showing Widened Grain Boundaries and Oxidized Fuel Rims

Particles 200 to 400 μm in diameter are chipped from the sample and embedded in epoxy within a small washer. The washer is thinned by grinding and ion-milling to produce a suitable sample. Examination is conducted in a 200 kV TEM using a small spot size. Selected area and microbeam electron diffraction are used for phase identification, diffraction contrast, and atomic lattice imaging for microstructural observation and energy dispersive x-ray spectrometry for compositional analysis.

During the Series 2 TGA tests(13) on PWR fuel, the TEM was used for observation of grain boundary conditions, phase identification at the oxidation boundary, and gas bubble and fission product location. A typical example of the phase identification is shown in Figure 2.2.

2.6 ANALYSIS OF DATA

The weight change data will be fit to existing models as described in the technical test description(4) and TGA test plan.(12) Oxidation rate constants will be determined as a function of temperature for the different mechanisms and combined with the TGA data to determine if there are new oxidation mechanisms appearing at low temperatures. The physical condition of the fuel as determined by ceramography, XRD, and electro-optical techniques will be correlated with the weight gains to determine the progression of the oxidation as a function of time. The models found to best fit the data will be used to extrapolate oxidation rates to repository temperatures, moisture conditions, and time.

2.7 PROCEDURES

Sample preparation, testing, and post-test evaluation will be conducted under approved procedures SFO-1-1, Rev. 1, "Sample Preparation for Spent Fuel Oxidation Testing Using a Dry Bath Heating System," and SFD-1-2, Rev. 1, "Measurement of Spent Fuel Oxidation Using a Dry Bath Heating System." Specific examinations will be conducted according to the procedures in Table 2.3.

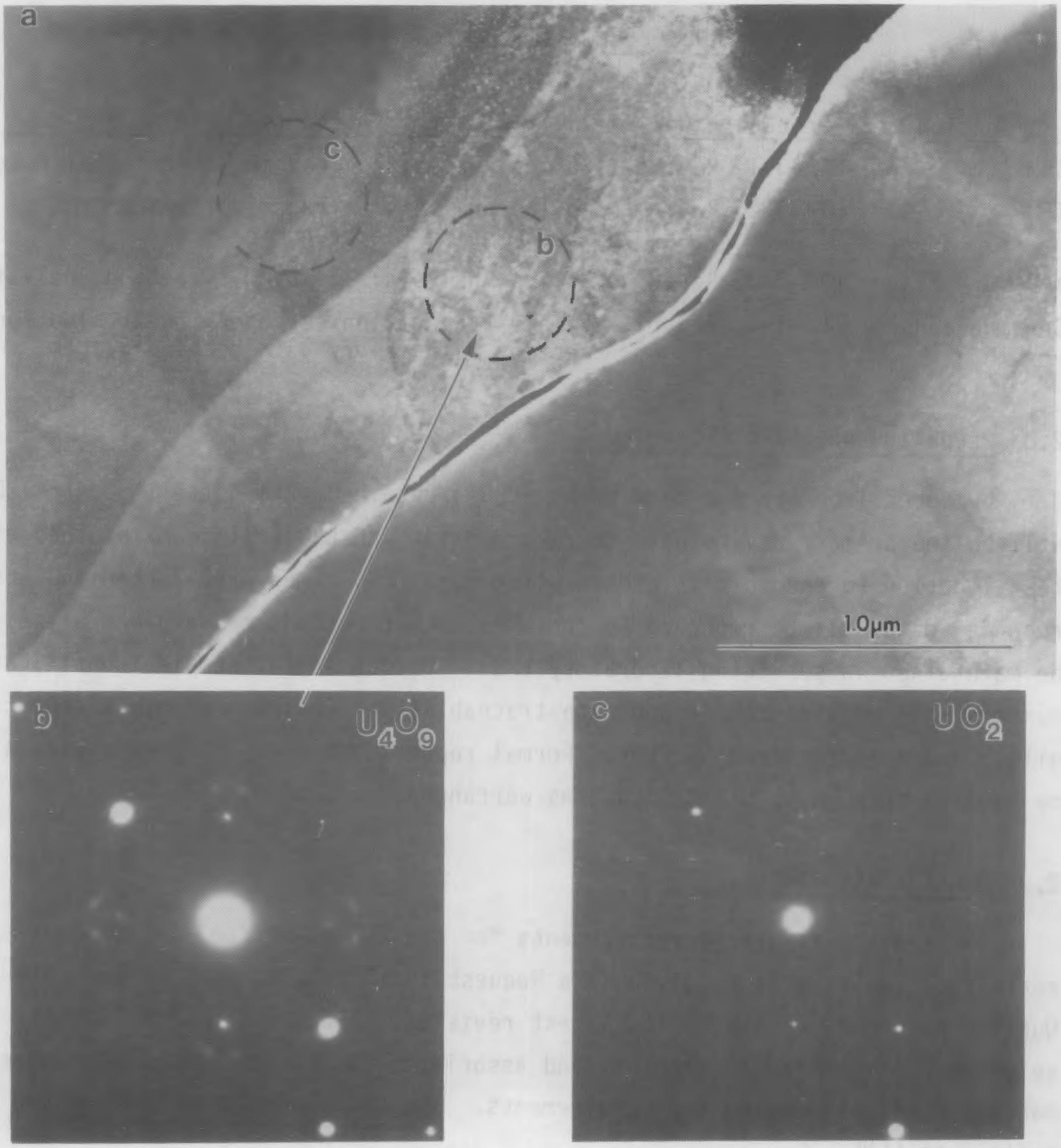

FIGURE 2.2. Grain Boundary Region in Oxidized Fuel. Sample G7-14-3-#8 (155°C test, O/M = 2.05). (a) Darkfield TEM taken with diffuse-scattered intensity from U_4O_9, showing enhanced intensity from U_4O_9 on one side of grain boundary. (b) Selected-area diffraction pattern from U_4O_9 region in (a), showing diffuse scattering from short-range ordered oxygen interstitials. Near (001) orientation. Arrow indicates aperture position used to form darkfield image (a). (c) SAD pattern for UO_2 region in (a). Same crystal orientation as (b).

TABLE 2.3. Examination Procedures

Examination	Procedure No.	Procedure Title
SEM	HTA-3-1, Rev. 4	Solids Analysis: Scanning Electron Microscopy
TEM	HTA-3-2, Rev. 4	Solids Analysis: Transmission/Scanning Transmission Electron Microscopy
XRD	HTA-3-3, Rev. 3	Solids Analysis: X-Ray Diffraction Analysis
Ceramography	SFO-1-1, Rev. 1	Sample Preparation for Spent Fuel Oxidation Testing Using a Dry Bath Heating System

2.8 REPORTING AND DATA RECORDING

Numbered laboratory record books (LRBs) obtained from Battelle Central Files will be the primary device used to record data. An LRB will be maintained at the test location to record test and sampling data. Specimen preparation and other recorded data will be recorded in the LRB. Other records on sample analyses will be maintained in servicing laboratory LRBs. Unique serial sample identification numbers will provide sample and data traceability. Periodic progress reports will be made as required by LLNL. Formal reports and open literature papers will be cleared through LLNL and issued as warranted.

2.9 QUALITY ASSURANCE

The quality assurance requirements for the TGA spent fuel oxidation testing activities, which will be given in a Request for Services, will be presented in a Quality Assurance Plan WTC-018, latest revision. The QA plan will identify the selected ANSI/ASME NQA-1 elements and associated PNL instructions, procedures and manuals for implementing the requirements. The QA plan will be transmitted in writing to LLNL.

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