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R. E. Einziger

December 1988

Prepared for
Lawrence Livermore National Laboratory
under a Related Services Agreement
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 additional low-temperature spent fuel oxidation data to determine the behavior of spent fuel as a waste form for a tuff repository. Short-term thermogravimetric analysis tests were recommended in a comprehensive technical approach as the method for providing scoping data that could be used to 1) evaluate the effects of variables such as moisture and burnup on the oxidation rate, 2) determine operative mechanisms, and 3) guide long-term, low-temperature oxidation testing. The initial test series studied the temperature and moisture effects on pressurized water reactor fuel as a function of particle and grain size. This document presents the test matrix for studying the oxidation behavior of boiling water reactor fuel in the temperature range of 140 to 225°C.

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FIGURES

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1.0 INTRODUCTION

The Yucca Mountain Project Office (YMPO) is evaluating 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. Studies(3,4) are under way at Pacific Northwest Laboratory (PNL)(a) to determine whether the spent fuel waste form helps meet these requirements by retarding the release of the radionuclides. The majority of spent fuel rods placed in a repository will consist of fragmented UO_2 pellets enclosed by intact Zircaloy cladding. A small fraction of the rods may have cladding defects, usually in the form of small splits or pinholes.(5) The spent fuel itself retards the release of some radionuclides, and the cladding provides a barrier by limiting the ingress of water to the fuel and the egress of radionuclides.

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. Analysis(6) of the standard free energies of the uranium oxides indicates that UO_2 may oxidize to higher states under the temperature and atmospheric conditions expected in a tuff repository. Further analyses also indicate that there will be sufficient air in the repository, at least initially, to exceed the equilibrium pressure necessary for the reactions. If the oxidation progresses far enough, the condition of the spent fuel could change,

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

affecting its ability to retain radionuclides. Swelling due to oxide formation may cause splitting of previously breached cladding, or significant quantities of higher oxides with potentially higher leach rates might form.

1.1 OBJECTIVE OF THERMOGRAVIMETRIC ANALYSIS TESTING

A technical approach(7) was developed to study spent fuel oxidation at the low temperatures characteristic of the post-container breach period. The approach, shown in Figure 1.1, is to perform tests and evaluations to gain understanding of the operative oxidation mechanisms, to obtain oxidation rate data, and to make projections of potential long-term spent fuel oxidation

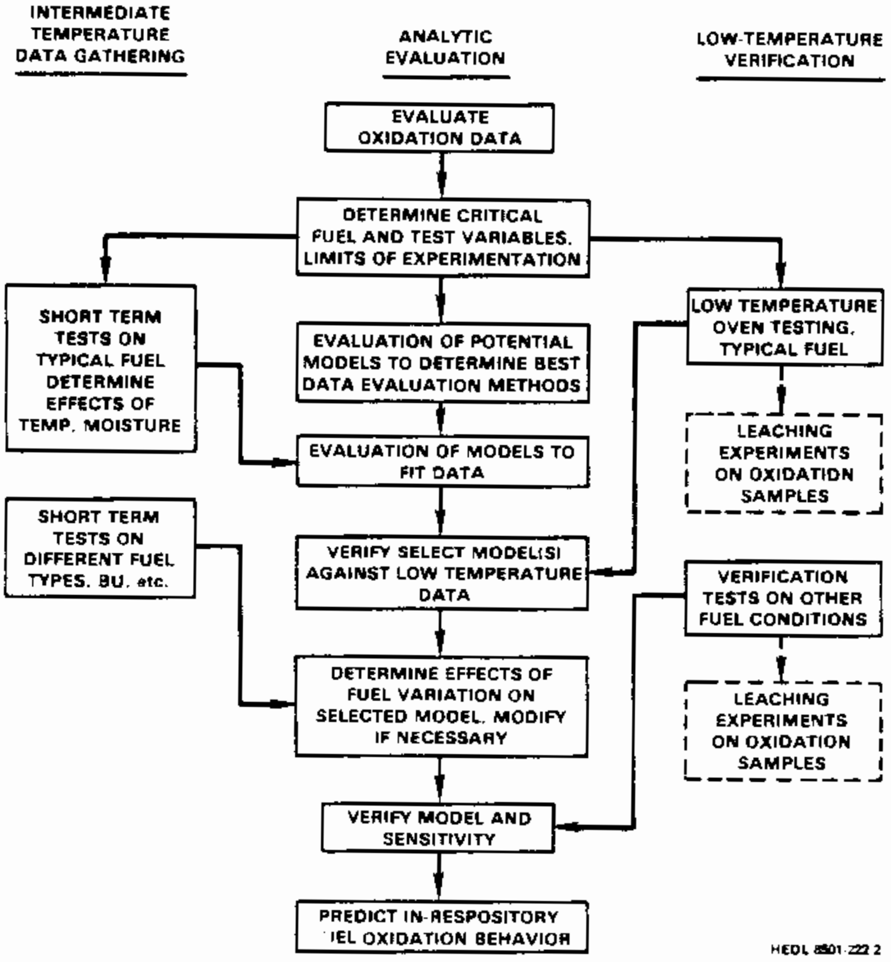

FIGURE 1.1. Technical Approach to Low-Temperature Fuel Oxidation Study

states. Time and temperature dependence of existing models are to be evaluated, and the dependence of the model projections on fuel variables will be determined. The objective of the short-term thermogravimetric analysis (TGA) is to determine, at intermediate temperatures where reaction rates are more rapid, important fuel characteristics (i.e., gas release, burnup, fuel type) and atmospheric variables (i.e., moisture content, radiation field) that affect the oxidation rate and influence the oxidation mechanism. The previous set of tests, Series 2, was designed to determine the effects of atmospheric moisture and temperature on the oxidation rate and phase formation in pressurized water reactor (PWR) spent fuel. The present series of tests are designed to determine only the temperature effects on the oxidation rate and phase formation in boiling water reactor (BWR) fuel. Grain size and particle size effects will not be investigated.

1.2 BACKGROUND

The spent fuel oxidation data base was extensively reviewed before the Series 2 tests. Based on the anticipated and possible atmospheres the rods might experience, several shortcomings in the data base were identified. The complete data evaluation, found in Reference 6, is summarized below. 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 a container might breach between 300 and 1000 years after repository closure, the spent fuel temperature$^{(8)}$ 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$^{(7)}$ of the high temperature data$^{(9)}$ indicates that insufficient spent 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 athermal fuel oxidation mechanisms taking place that are insignificant at the higher test temperatures but that become dominant at the lower temperatures expected in the repository. These extrapolations are based on oxidation data from PWR spent fuel using laboratory air with its normal moisture content. The effect of the moisture content of the air and the validity of using PWR spent fuel oxidation data for BWR spent fuel performance predictions are unknown.

Recent oxidation studies have been performed in Canada and the United States at temperatures below 200°C with a range of moisture in the atmosphere. CANDU spent fuel, with a high linear heat rating, showed a strong enhancement of grain boundary attack in a saturated moist atmosphere(a) at 150°C.(10) Gilbert et al.(11) have studied the oxidation of a variety of spent fuels over a range of burnups. In the range of 10 to 35 GWd/MTU, burnup had little effect on the oxidation rate of Quad Cities BWR fuel at 230°C. Monticello experimental BWR-rodlet spent fuel showed as much as 2% weight gain, equivalent to U_3O_7, in only 6000 h at 170°C, although the uncertainty was as much as 50%.(11) Little difference was found between the behavior of BWR and PWR fuel. The efforts of that BWR study(11) and its companion PWR studies(11) were aimed more at determining powder formation applicable to dry storage than mechanisms of U_3O_7 and U_4O_9 formation applicable to repository work. These BWR and PWR studies were also conducted in a high flux (5×10^5 R/h) imposed gamma field, which would not be present in the repository at the expected time of possible container failure.

The TGA study of Turkey Point PWR spent fuel(11) between 225°C and 140°C indicated that oxidation appears to occur by a two-stage mechanism: 1) diffusion of oxygen into and oxidation of the grain boundaries, and 2) bulk oxidation of the grains by the progression of a U_4O_9/UO_2 front due to diffusion of O_2 through a layer of oxygen-saturated U_4O_9. Particle size would be unimportant if the grain boundary diffusion occurs rapidly with respect to the test duration. However, the TGA test at 140°C indicated that it is necessary to use pulverized fuel to obtain measurable oxidation in a reasonable length of time, since grain boundary diffusion is very slow at the lower temperatures.

(a) Reference 10 was ambiguous with respect to the meaning of saturated moist atmosphere.

Over a range of 3 to 16,000 ppm of H_2O, the moisture content of the air appears to have only a minor effect on the short-term oxidation rate of PWR fuel.(12) The rate may decrease with increasing moisture content.(12)

2.0 EXPERIMENTAL DESCRIPTION

The tests described in this test plan will be conducted in a TGA system that provides the proper atmosphere and temperature and records the sample weight gain as a function of time. The samples will come from BWR fuel rods that are being characterized by the Materials Characterization Center (MCC) at PNL. The general procedure for oxidation tests is as follows: 1) maintain the sample under the proper environmental conditions, 2) heat the sample to the desired temperature, 3) determine a measure of the oxidation, usually weight gain or phase change, and 4) monitor the oxidation as a function of time. This can be repeated for as many sample types, environments, and temperatures as is practical. Basically, a sample, an environment, a heating source, and a response measurement are needed. After the tests are complete, the samples will be further examined by techniques such as x-ray diffraction (XRD), ceramography, transmission electron microscopy (TEM), ion-microprobe, and scanning electron microscopy (SEM). The gas mixture in the system will be monitored for ^{85}Kr. The data will be compared with the TGA oxidation data obtained on PWR fuel(12) and long-term tests conducted in drybaths.(13)

2.1 TEST MATRIX

The BWR fuel oxidation test matrix as shown in Table 2.1 consists of ten subtests at five temperatures with an atmospheric dew point of 14.5°C. Temperatures will range from 140 to 225°C and tests will last from 300 to 3000 h.

The BWR fuel oxidation rate is expected to have an Arrhenius temperature behavior similar to that exhibited by the PWR fuel. It would be desirable to have oxidation data at repository temperatures, ~100°C, however, the TGA system cannot provide useful information in a reasonable length of time below 140°C because the quality of the data is marginal at best. In order to make direct comparison with the oxidation results on PWR fuel, test temperatures of 225, 200, 175, 155, and 140°C were chosen. These temperatures nearly equally divide the reciprocal temperature range of interest.

TABLE 2.1. TGA BWR Fuel Test Matrix

Test	Nominal Temperature (°C)	Fuel	Nominal Moisture (DP)	Sample Condition	Tentative Test Duration (h)
BWR-1	200	Cooper	+14.5	fragment	800
BWR-2	155	Cooper	+14.5	fragment	2200
BWR-3	225	Cooper	+14.5	fragment	300-600
BWR-4	175	Cooper	+14.5	fragment	2100
BWR-5	140	Cooper	+14.5	pulverized	3000
BWR-6	225	Cooper	+14.5	fragment	300-600
BWR-7	155	Cooper	+14.5	fragment	2200
BWR-8	200	Cooper	+14.5	fragment	800
BWR-9	175	Cooper	+14.5	pulverized	2100
BWR-10	155	Cooper	+14.5	pulverized	2200

No external radiation field will be imposed on the samples. The spent fuel will be subjected to its own radiation field generated by the self-contained fission products and actinides. This self-gamma field, depending on whether the fuel was fragmented or pulverized, ranges from 5 to 10% of the gamma field that the fuel would have seen if the fuel were in an assembly configuration but 800 to 1500 times greater than expected in 300- to 1000-year-old fuel.(6,14,15) Therefore, the fragment test sample will have a self-gamma field that is over 30 times greater than that experienced by spent fuel in an assembly after 300 years. Due to the short range, limited mobility, and long half-life of the actinide elements, the alpha field is similar to that which would be expected in the repository. Therefore, no external fields are needed to simulate low-temperature repository conditions. We are aware that the higher fields in younger fuel may produce higher oxidation rates in the test fuel than would occur in spent fuel stored for 1000 years in a repository.

The test atmosphere will be 80% N_2 + 20% $^{18}O_2$ with a dewpoint of +14.5°C. The $^{18}O_2$ atmosphere was chosen so that post-test ion-microprobe examinations can be used to distinguish between the oxidizing ^{18}O species and normal ^{16}O in the UO_2. While the Canadian studies on CANDU fuel with a high linear heat rating indicated an enhancement of grain boundary oxidation in a water-saturated atmosphere relative to a dry atmosphere at 150°C, both TGA tests on PWR fuel between 140°C and 225°C and drybath oxidation tests between 175°C and 110°C have shown that atmospheric moisture in the range of ~3 to ~400,000 ppm H_2O has little influence on oxidation rates. However, if there is a moisture effect, the oxidation rate of low-gas-release PWR fuel is reduced as the moisture level increases. Therefore, this series of tests on BWR spent fuel will only be conducted at a dewpoint of 14.5°C; this condition is easy to establish, is the same dewpoint used in a majority of the PWR tests, and should provide an upper bound for the oxidation rate at a dewpoint of 95°C. Tests at other dewpoints, as low as -70°C, can be conducted if it is deemed necessary. The effect of the moisture content of the atmosphere is being examined in a parallel series of BWR spent fuel oxidation tests using a drybath apparatus.(16)

The Series 2 TGA tests on PWR spent fuel and drybath tests on PWR spent fuel have shown that below 175°C the oxidation rate observed in the test and particle size are interdependent. The test duration and particle size combinations in the matrix were chosen to give measurable oxidation results. Based on the PWR fuel TGA tests, no measurable weight gain should occur on a fragment sample after 3000 h at 140°C, but a pulverized sample would yield a measurable weight gain. Tests on pulverized fuel will also be conducted at 155°C and 175°C to compare the results with those from tests using fragment samples.

Tests BWR-1 through BWR-5 represent the basic BWR series and are the minimum testing needed for comparison of BWR and PWR spent fuel oxidation behavior. Given the typical scatter seen in the PWR tests, a much more convincing comparison could be made if the three replicate tests are also conducted. The matrix is predicated on the expectation that BWR and PWR fuel will behave similarly. If this turns out not to be the case, then the test matrix will have to be readjusted.

2.2 SAMPLE PREPARATION AND IDENTIFICATION

2.2.1 Test Fuel Selection

BWR 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. The published characteristics of the assembly are given in Table 2.2 and are thought to be representative of an average

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	~0.6%
Initial Enrichment	2.93%
Initial Pellet Density	10.42 g/cm^3
Initial Rod Diameter	1.42 cm
Cladding Material	Zircaloy-2
Cladding Thickness	0.081 cm
Rod Identification	ADD-2974

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

burnup, low fission gas release BWR fuel. Samples for these TGA tests and companion long-term drybath tests will come from rod ADD-2974 in position 3C. The history of this rod will be described in a report shortly to be released by the MCC. The ATM-105 fuel assembly contains four types of spent fuel rods: 1) 2.93% ^{235}U enrichment, 2) 1.94% ^{235}U enrichment, 3) 1.94% ^{235}U enrichment plus 4 wt% Gd_2O_3, and 4) 2.93% ^{235}U 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.

The MCC will characterize the rods. Before 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 done adjacent to the burnup samples to determine grain size and look for unusual features.

After the cladding is slit, 10 to 20 fragments of ~200 mg or less each will be removed from one end of the rod segment and placed in a vial for transfer to the 325 Building for use in the TGA experiments. Further characterization by XRD, TEM, electron diffraction, and SEM will be conducted if similar examinations were not performed by MCC. A test sample will consist of either one or two fragments weighing approximately 200 mg or, in the case of BWR-5, BWR-9 and BWR-10 tests, fuel pulverized to -10/+24 Tyler mesh (i.e., 1.7 to 0.7 mm). Before testing, the fragment(s) will be photographed in order to document whether it came from the pellet surface and to determine an approximate size. The sample will be weighed to ±0.01 mg before placement in the TGA system.

2.2.2 Sample Identification

Each sample will be identified by the ATM number, rod number, elevation on the rod, and an assigned sample identification letter. The identification would thus appear as: ATM-rod-elevation-N.

2.3 TESTING ATMOSPHERE

The spent fuel is expected to contact a water-saturated moist-air atmosphere after container and cladding breach in the tuff repository. The oxygen in UO_2 has normal isotopic composition and is almost totally ^{16}O. If testing were conducted in a natural air atmosphere, there would be no way to distinguish the location of the additional oxygen in the reaction product UO_{2+X}. For diagnostic purposes, a mixture of 80% N_2 plus 20% $^{18}O_2$ will be used as a testing atmosphere instead of air. Since the ion microprobe can readily distinguish ^{18}O from ^{16}O, it is possible that post-test examination of the sample will give a clue to the location in the sample where oxidation is taking place. Before the start of the test series, the $^{18}O_2$ source will be analyzed to determine its purity with respect to $^{16}O_2$. The recirculated atmospheric flow will be approximately 500 cc/min, sufficient to keep an ample O_2 supply around the sample and yet not cause buoyancy effects or undue vibration to the sample.

In a repository 1000 years after closure, an atmosphere with a dewpoint near 95°C may be encountered. The highest dewpoint achievable in the TGA system is 20°C because the whole TGA microbalance is not in a thermostatically controlled environment. The moisture level will be maintained by a refrigerated bath, which circulates a coolant through coils surrounding a trap that contains the water source. The trap temperature, which is monitored continuously, establishes the dewpoint of the gas flowing through the trap.

2.4 THERMOGRAVIMETRIC ANALYSIS SYSTEM

A TGA apparatus consists of a system to establish a controlled atmosphere with the correct moisture content, a furnace to heat the sample, and an analytical balance to weigh the fuel sample continuously while it is at temperature in the furnace (see Figure 2.1). The apparatus is excellent for continuously measuring small weight changes resulting from oxidation. The samples must be weighed before and after testing to confirm the measured weight change.

Spent fuel oxidation testing to date using a unit of this type has shown excellent temperature and weighing stability for periods up to 2100 h, possibly due to neutralization of static charges by the ionizing radiation field. The stability can probably be maintained for longer periods of time. The furnace can be controlled to ±1°C at temperatures up to 300°C. There are limitations on the sample size, moisture content in the atmosphere, and radiation field that the unit is capable of accommodating. The radiation limits in the open hood limit the sample size to no more than ~200 mg of spent fuel, which is equivalent to an average spent fuel fragment. A weight change of 0.01%, equivalent to 20 μg is well above the stability and sensitivity limits of the microbalance. A complete sample conversion to U_3O_7 amounts to ~2% or 4 mg. The system can accommodate only one sample at a time.

All measurement instrumentation (i.e., balances, thermocouples, and data recorders) will be calibrated against National Institute of Standards and Technology (NIST) traceable reference standards such as voltage, mass, or melting points. Calibration records, along with either copies of the calibration procedures or traceable reference to the calibration procedures, will be included in the data package for this test series. The frequency of calibration will be at the discretion of the principle investigator, but as a minimum at least prior to and after the test series.

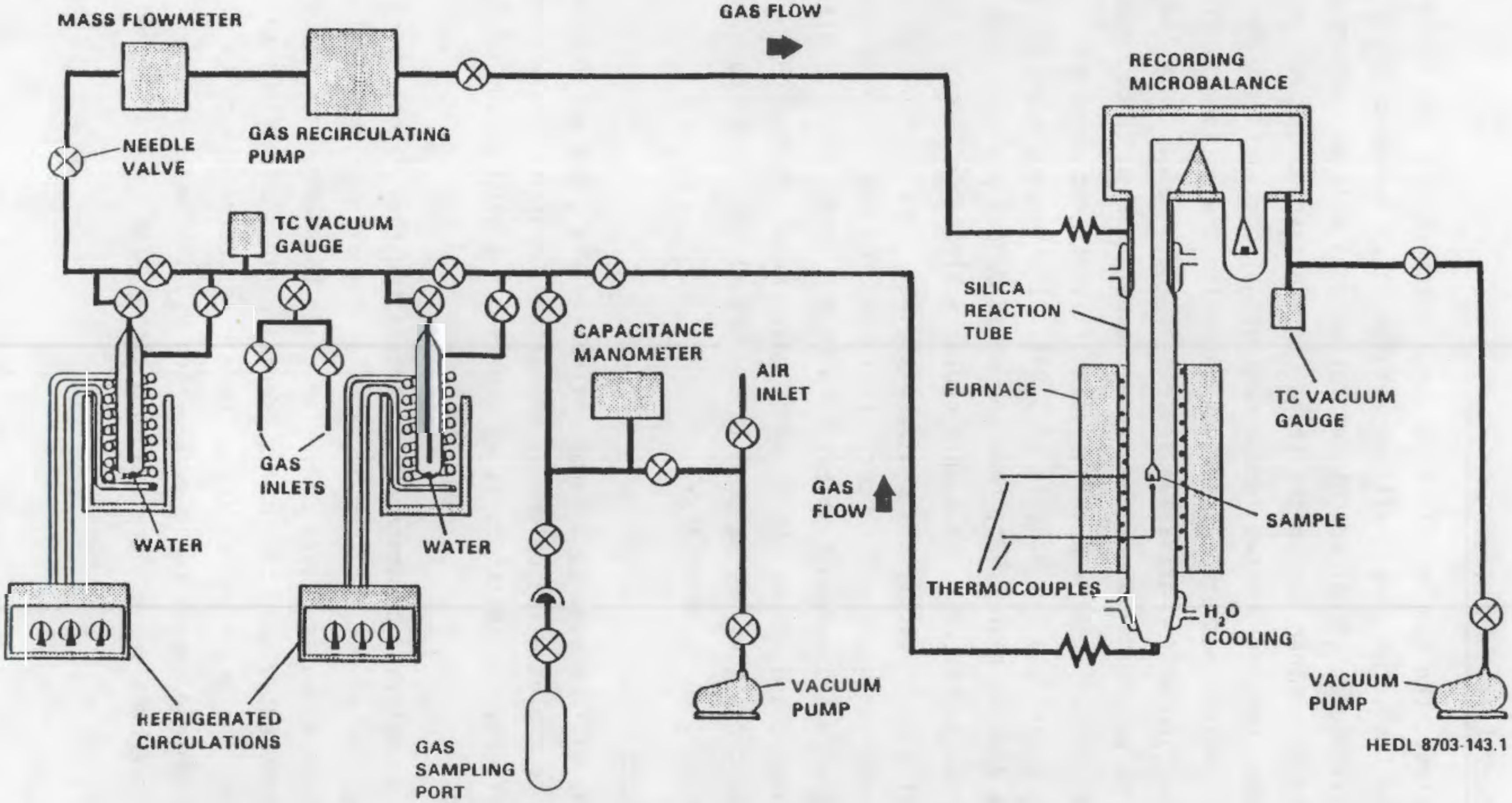

FIGURE 2.1. Schematic of TGA System

2.5 POST-TEST SAMPLE AND GAS EVALUATION

During the test, the sample will be weighed automatically and continuously. After the test, the sample will be weighed on an independent balance and the weight difference (final weight-initial weight) will be compared with the weight change determined during the test. In the past, there has been excellent agreement between the two independent weight checks in the PWR fuel oxidation tests. 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 were found to be greater than 1.98%, then one would probably assume that at least some U_3O_8 had formed, but the sample could be almost uniformly U_3O_7 with a minor amount of U_3O_8 or partly UO_2 and partly U_3O_8. In all likelihood, some of all three phases would probably occur. Following the test, the samples selected will be examined ceramographically, with SEM, TEM, electron diffraction, ion microprobe, and XRD to obtain additional phase information. Other, more experimental techniques may be used if the established techniques indicate that further examination is necessary.

2.5.1 Ceramography

Ceramography will be used to determine visually 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.

Typically, as-polished ceramography of irradiated fuel reveals very little grain structure. The as-polished ceramographs of the oxidized PWR fuel were quite different, as shown in Figure 2.2. The grain boundaries are quite noticeable and widened; within the grains there are rings of various thicknesses paralleling 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.

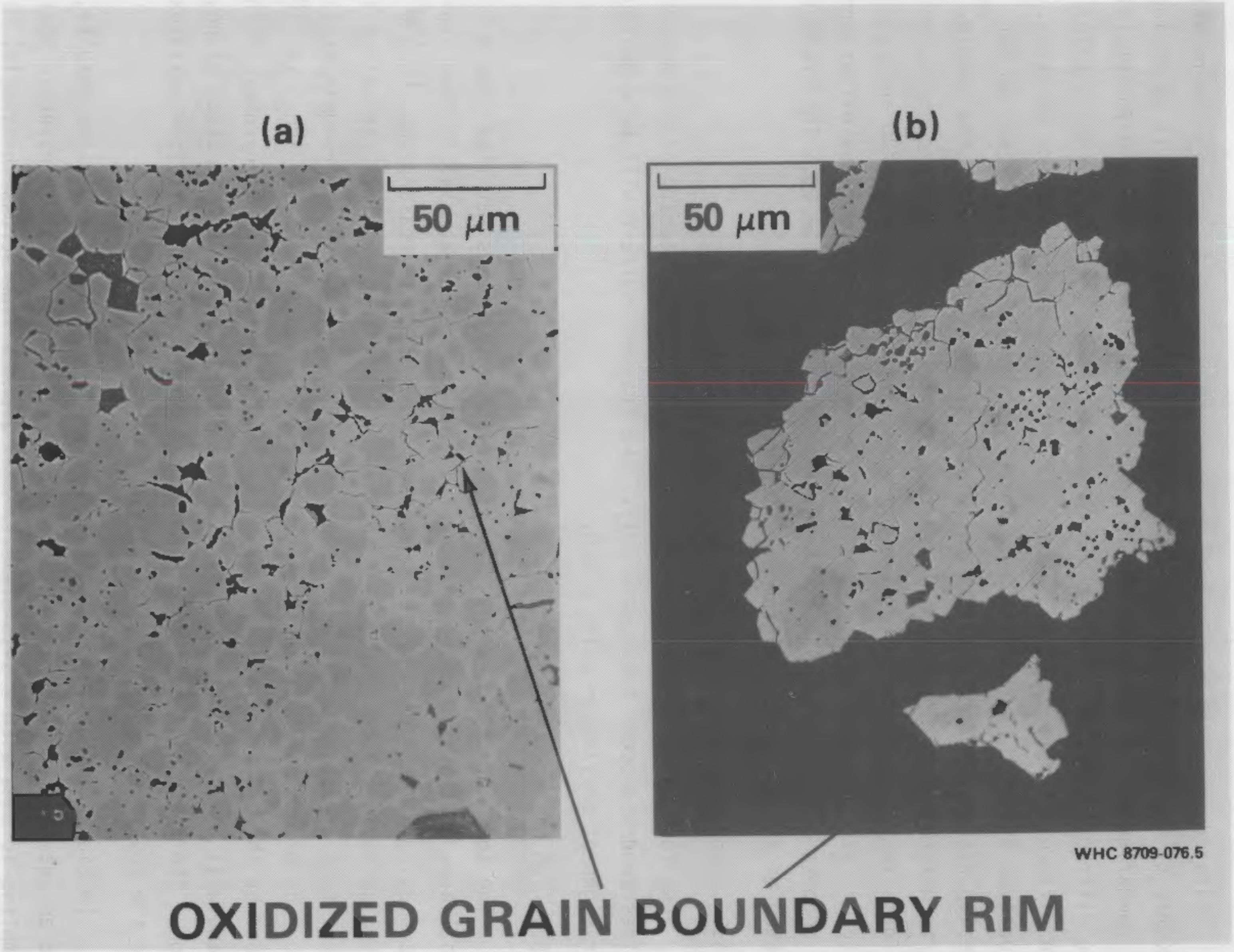

FIGURE 2.2. As-Polished Ceramography of Oxidized Fuel Showing Widened Grain Boundaries and Oxidized Fuel Runs: a) Run 15 at 175°C, b) Run 1 at 225°C

2.5.2 X-Ray Diffraction

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 silver, which has diffraction lines that do not overlap with those of the various uranium oxides, is included in the sample. X-ray diffractometers sample an area that is much greater than one grain, so no information can be obtained on the oxide distribution. Careful XRD 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%. The preferred method of XRD utilizes fuel samples prepared by grinding.

2.5.3 Scanning Electron Microscopy

LWR fuel tends to fracture intragranularly, but spallation of the higher oxides tends to occur intergranularly. The fragment surface will be examined for signs of spallation using a SEM.

2.5.4 Ion Microprobe

The ion microprobe, using $^{16}O_2$ primary beam, sputters material from a small area on the surface of the sample. The sputtered material is then analyzed using a mass spectrometer. It can thus be used to measure the $^{18}O/^{16}O$ ratio at various locations on the surface of a polished sample. The oxides in spent fuel are composed of uranium and normal oxygen, which is predominantly ^{16}O. By oxidizing the spent fuel samples in a mixture of N_2 and $^{18}O_2$, the ^{18}O added by the oxidation process can be identified by the ion microprobe. Point scans will be used to try to determine the $^{18}O/^{16}O$ ratio as a function of position. The ratio will help to determine the location of the oxidized surfaces and the possible oxide composition, i.e., $U^{16}O_2{}^{18}O_X$.

Initial examinations of two PWR fuel samples have yielded mixed results, and as yet the technique can only be considered experimental in nature. Spot sampling is done with a 6-μm-diameter beam along a line across the sample. The location of the beam relative to the outer sample surface and local grain boundary are carefully noted. The results of one such line scan from oxidized PWR fuel are shown in Figure 2.3. It seems to clearly indicate more oxidation on the grain boundaries as opposed to the grain interior. It also seems to indicate the presence of higher oxides such as UO_3 and U_3O_8 on the grain boundaries, but this interpretation is not conclusive when the results from the electron diffraction and XRD measurements are analyzed.$^{(12)}$ Diffusional interchange of the ^{18}O and ^{16}O may be confusing the interpretation of the ratio of $^{18}O/(^{16}O + ^{18}O)$, which could theoretically approach 1 if there were complete exchange of the oxygen initially in the fuel with the ^{18}O in the TGA atmosphere.

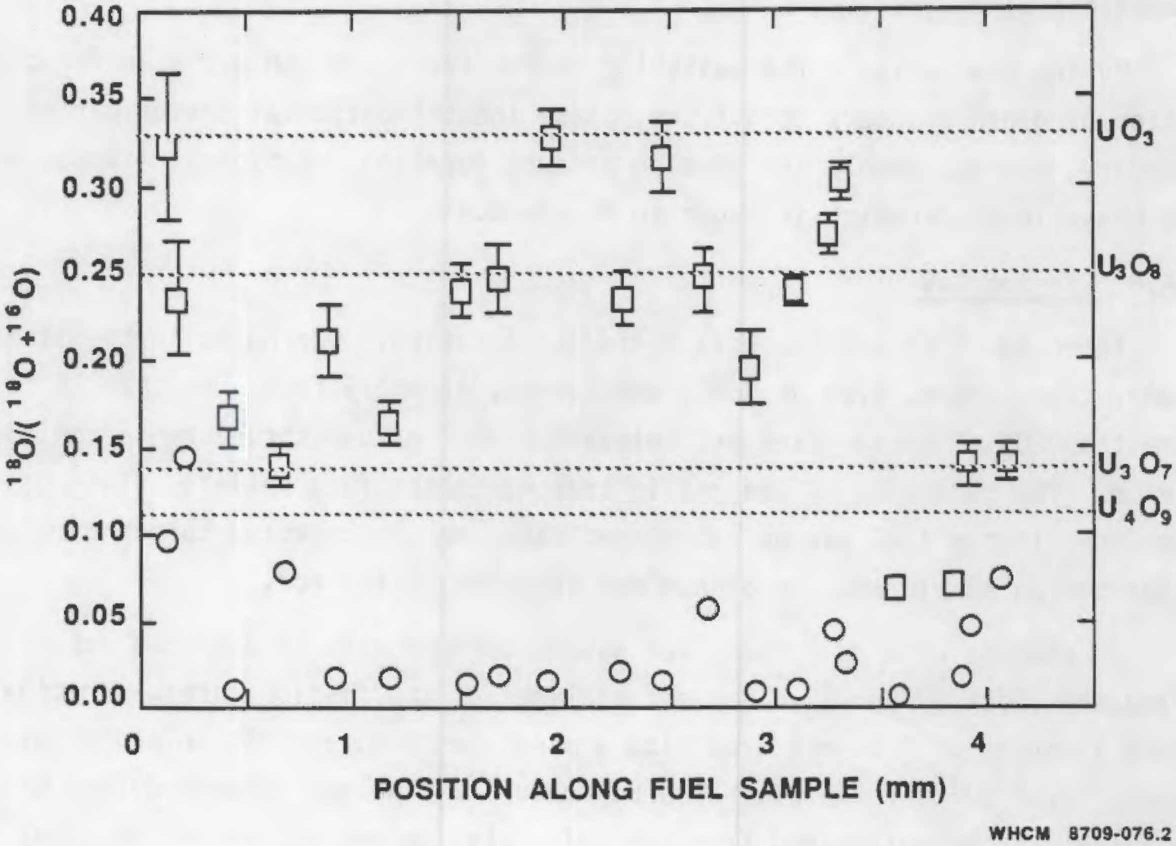

FIGURE 2.3. ^{18}O Distribution in PWR Fuel Oxidized at 175.6°C. Squares are at grain boundaries and circles are at grain centers.

2.5.5 Transmission Electron Microscopy 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.

Particles 200 to 400 μm in diameter are chipped from the sample and embeded 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(12) 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 2.4.

2.5.6 Fission Gas

Xenon and ^{85}Kr are produced during irradiation. Depending on the linear power, temperature, type of fuel, and burnup, anywhere from less than 1% to more than 20% of these gases are released from the fuel structure to the rod plenum. The remainder of the gas is trapped in the fuel pellets. This gas entrained in the fuel can be calculated based on the measured burnup of a characterization sample and the plenum gas analyses of the rod.

At the end of a run, the cover gas atmosphere will be expanded into an evacuated flask of known volume for analyses of the fission gases. Krypton and xenon isotopes will be measured with a mass spectrometer. As an additional check, the $^{18}O/^{16}O$ ratio will also be measured. The gas release during the oxidation can be determined from the calculated gas entrained in the spent fuel and the fission gas measured after the oxidation test.

Fission gas released from the PWR spent fuel during TGA oxidation tests was generally less than 1%. This was expected, since no bulk U_3O_8 was found and hence there was no lattice disruption to release the gas. Oxidation to

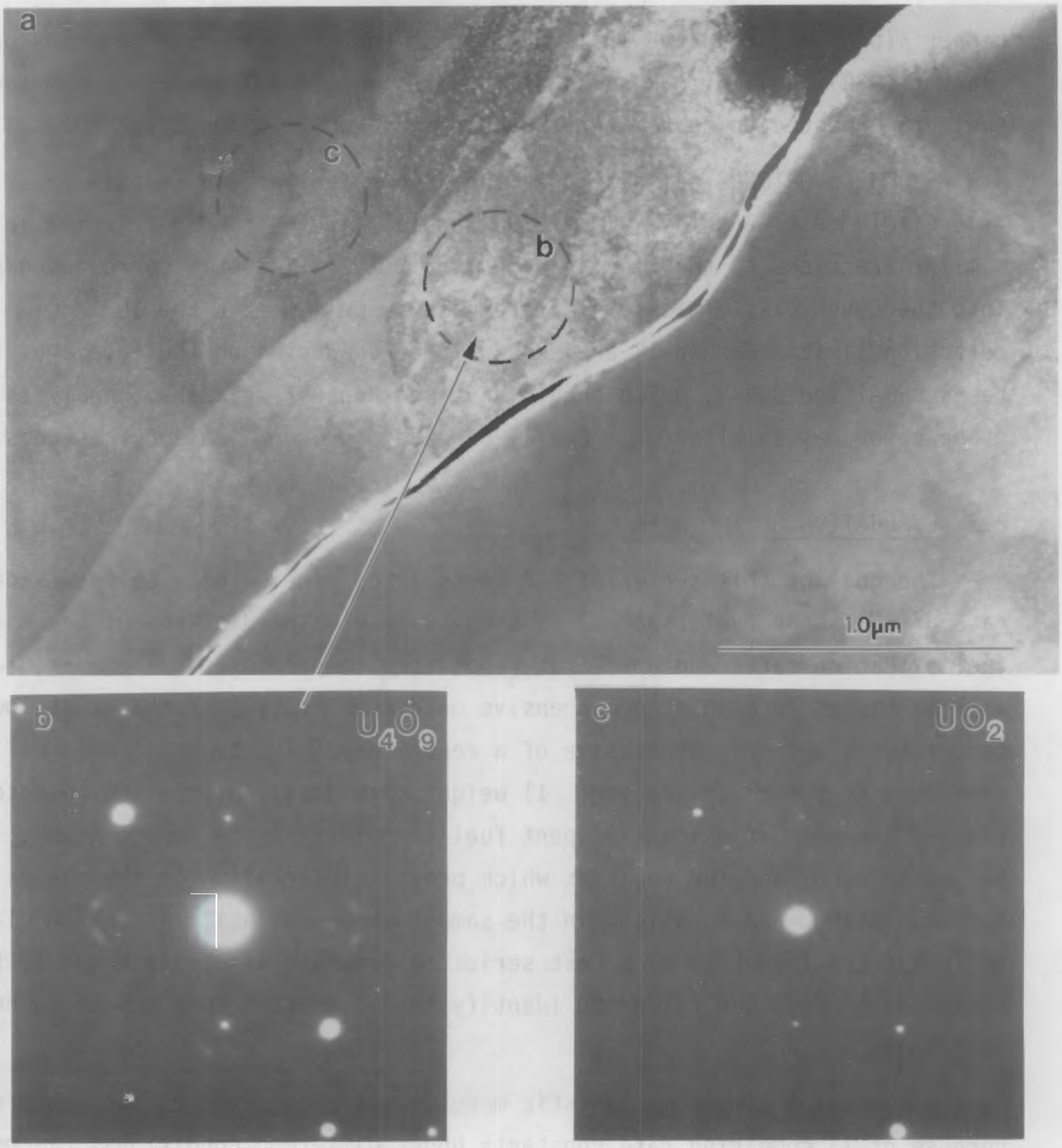

FIGURE 2.4. Grain Boundary Region in Oxidized Fuel. Sample G7-14-3-#8 (155°C test, O/M = 2.05). (a) Darkfield TEM taken with diffuse-scattered intensity from U_4O_9, showing enhanced intensity from U_4O_9 on one side of grain boundary. Only one side of the grain boundary could be imaged at a time. (b) 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) Selected area diffraction (SAD) pattern from UO_2 region in (a). Same crystal orientation as (b).

higher $\Delta(O/M)$ has resulted in large fission gas releases from advanced gas reactor (AGR) fuel.(17) Results of the fission gas releases from BWR spent fuel are expected to be similar to those measured from PWR spent fuel.

Based on ORIGEN2 calculations, the Cooper fuel should contain ~1.5 Ci/MTHM, or ~3 x 10^{-7} Ci per TGA sample. If the ^{14}C is released in similar fractions to the fission gases, ~3 x 10^{-9} Ci should be released per run into the cover gas. This level of release is well within the 10^{-10} Ci detection limit. Carbon-14 analyses will be conducted on the cover gas from tests BWR-1 and BWR-3, which should have the highest releases. Analyses of other cover gas samples for ^{14}C will be determined on a case by case basis.

2.6 EVALUATION OF THE DATA

The goal of this series of TGA tests is to provide data on the oxidation rate of BWR spent fuel that can be used to develop predictions of the spent fuel oxidation rates and phases at repository temperatures. These predictions will be tested in a more comprehensive matrix of tests in furnaces at lower temperatures more representative of a repository. Two types of data will be available from the TGA testing: 1) weight gain data, which allows a determination of the rate at which the spent fuel is oxidizing, 2) ceramography, TEM, ion microprobe, and XRD analyses which provide information on the phases that are developing, and locations in the sample where oxidation is taking place. It is not the intent of this test series to generate independent models for the oxidation process but rather to identify the mechanisms that appear to be operating.

A number of simple mechanistic models will be applied to the data for the purpose of 1) comparing rate constants under different conditions, 2) comparing PWR versus BWR fuel, and 3) determining the effect of experimental uncertainty on repository predictions.

Examination of the ceramography, ion-microprobe, and TEM data from the PWR samples of Series 2(12) reveals that oxidation may be occurring by rapid diffusion along the grain boundaries followed by slow bulk diffusion through a layer of oxygen-saturated U_4O_9. When the data was fit to a model of diffusion through a layer as the rate-controlling step (see Figure 2.5), there was an

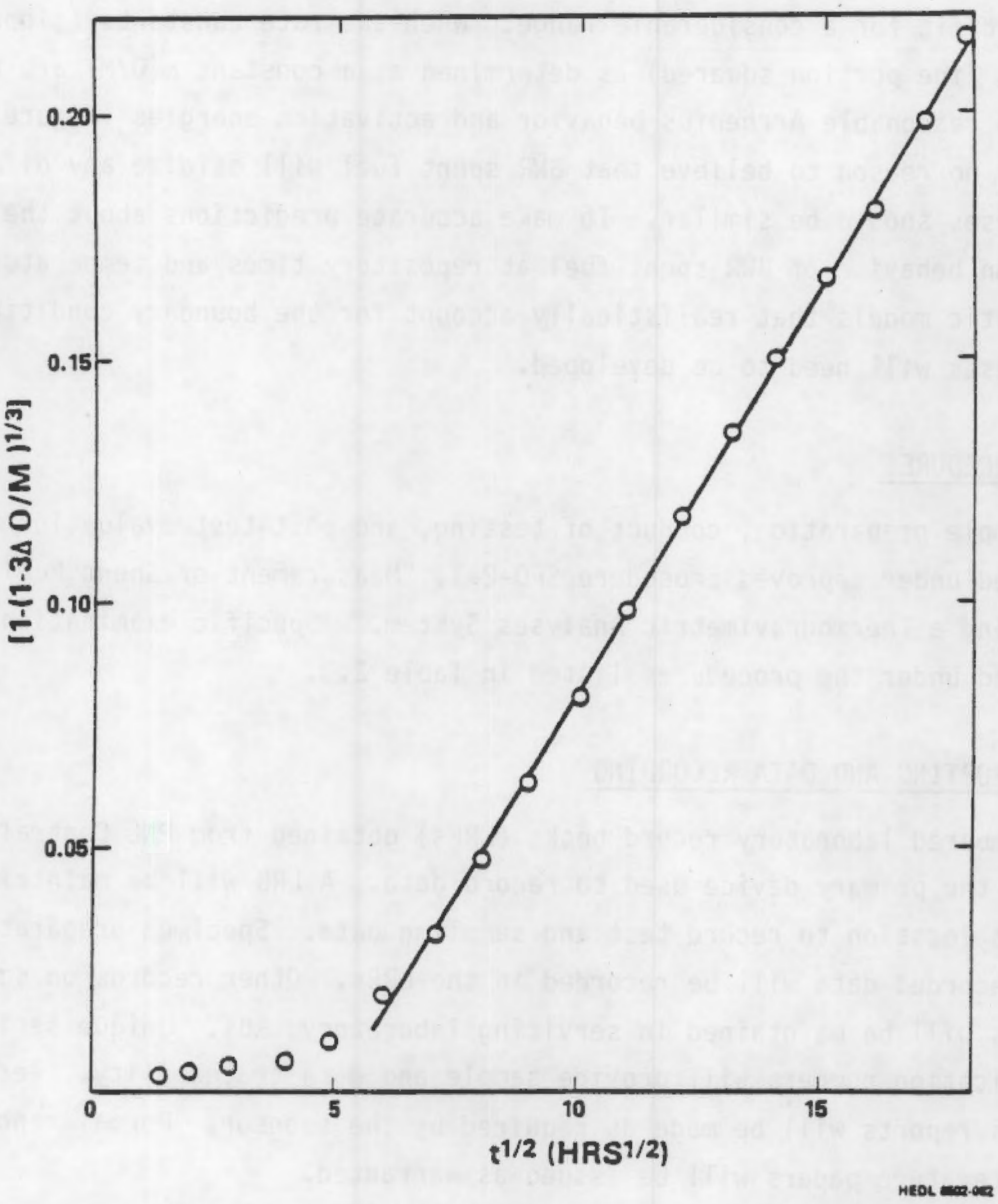

FIGURE 2.5. Oxidation of Spent Turkey Point PWR Fuel in Air at 200°C. Measurement error on the data is less than ±5% at any point. If diffusion through a layer of UO_2 oxidized to the composition of U_3O_7 is rate controlling, then the plot of $[1-(1-3\Delta(O/M))^{1/3}]$ vs $t^{1/2}$ should be a straight line with the slope being the square root of the rate constant.

excellent fit for a considerable range. When the rate constants (slope of the straight line portion squared) as determined at a constant $\Delta(O/M)$ are compared, there is reasonable Arrhenius behavior and activation energies (Figure 2.6). There is no reason to believe that BWR spent fuel will oxidize any differently, so analyses should be similar. To make accurate predictions about the oxidation behavior of BWR spent fuel at repository times and temperatures, mechanistic models that realistically account for the boundary conditions in these tests will need to be developed.

2.7 PROCEDURES

Sample preparation, conduct of testing, and post-test evaluation will be conducted under approved procedure SFO-2-1, "Measurement of Spent Fuel Oxidation Using a Thermogravimetric Analyses System." Specific examinations will be conducted under the procedures listed in Table 2.3.

2.8 REPORTING AND DATA RECORDING

Numbered laboratory record books (LRBs) obtained from PNL Central Files will be the primary device used to record data. A 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 LRBs. 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 the sponsor. Formal reports and open literature papers will be issued as warranted.

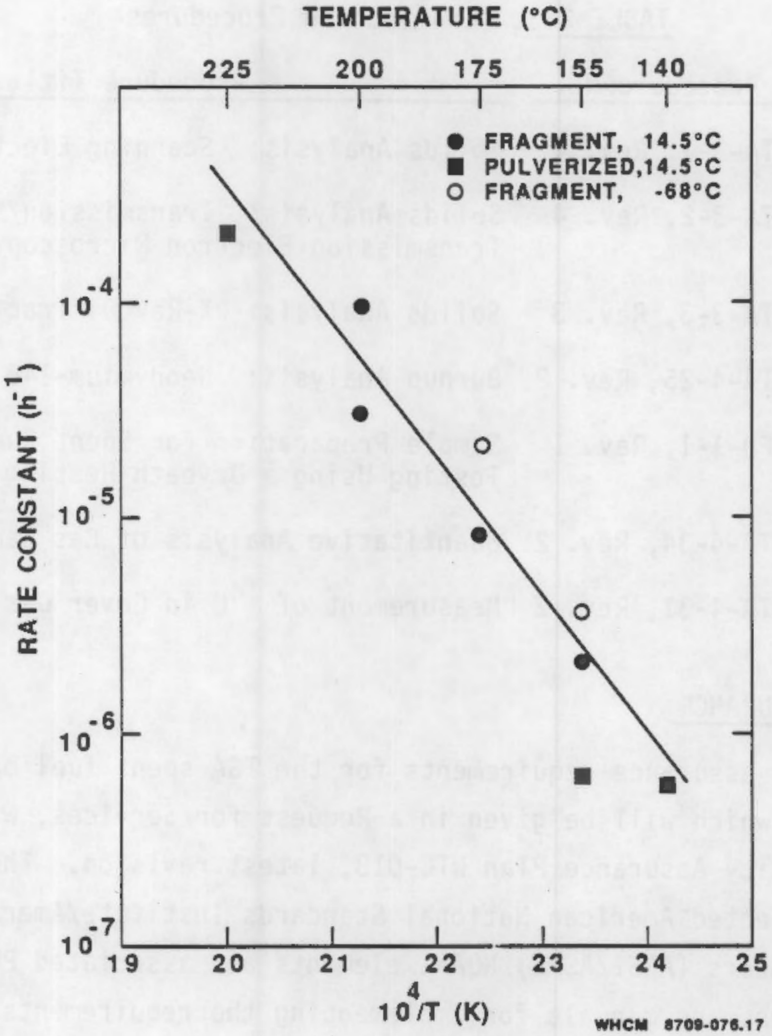

FIGURE 2.6. Arrhenius Plot at Δ(O/M) = 0.02 for Oxidation of PWR Fuel

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
Burnup	HTA-4-25, Rev. 2	Burnup Analysis: Neodymium-148 Method
Ceramography	SFO-1-1, Rev. 1	Sample Preparation for Spent Fuel Oxidation Testing Using a Drybath Heating System
Gas Analysis	HTA-4-34, Rev. 2	Quantitative Analysis of Gas Samples
^{14}C	HTA-4-31, Rev. 2	Measurement of ^{14}C in Cover Gas

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 American National Standards Institute/American Society of Mechanical Engineers (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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