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LOW TEMPERATURE SPENT FUEL OXIDATION UNDER TUFF REPOSITORY CONDITIONS

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ABSTRACT

The Nevada Nuclear Waste Storage Investigations Project is studying the suitability of tuffaceous rocks at Yucca Mountain, Nye County, Nevada, for high level waste disposal. The oxidation state of LWR spent fuel in a tuff repository may be a significant factor in determining its ability to inhibit radionuclide migration. Long term exposure at low temperatures to the moist air expected in a tuff repository is expected to increase the oxidation state of the fuel. A program is underway to determine the spent fuel oxidation mechanisms which might be active in a tuff repository. Initial work involves a series of TGA experiments to determine the effectiveness of the technique and to obtain preliminary oxidation data. Tests were run at 200° and 225°C for as long as 720 hours. Grain boundary diffusion appears to open up a greater surface area for oxidation prior to the onset of bulk diffusion. Temperature strongly influences the oxidation rates. The effect of moisture is small but readily measurable.

INTRODUCTION

Spent LWR fuel consists primarily of UO_2 pellets enclosed in a Zircaloy sheath. Although the vast majority of the spent fuel rods placed in a tuff repository will have intact Zircaloy cladding, approximately 0.01% of the rods may contain cladding defects, usually in the form of small splits or pin holes.[1] EPA and NRC have established requirements[2,3] limiting potential radionuclide release. Studies[4,5] are underway to determine if the spent fuel waste form will help meet these requirements by providing a barrier to radionuclide release after ground water enters the spent fuel canister. The fuel pellet provides a barrier if the leach rate is sufficiently low, and the cladding could provide a barrier by limiting the ingress of water to the fuel pellet and egress of radionuclides. If cladding with small breaches provides a barrier function, then it will be necessary to determine if fuel oxidation splits the cladding and exposes an increasing amount of fuel with an oxidation state higher than UO_2. The oxidation state of the waste form may also affect its ability to act as a barrier to radionuclide release.

When UO_2 oxidizes, it passes through certain metastable states, such as U_3O_7 and U_3O_8, before it is totally oxidized to UO_3. Its rate of oxidation depends on the temperature and may also depend on the moisture content of the atmosphere, previous irradiation history of the fuel and radiation level during storage. The densities of the oxides range from a high of 10.3 g/cm^3 for 94% dense UO_2 to 7.3 g/cm^3 for UO_3. Until U_3O_8 with a density of 8.3 g/cm^3 is formed, intermediate phases, U_3O_7 and U_4O_9, have densities slightly higher than UO_2. Therefore, as the UO_2 oxidizes through U_3O_8, the fuel pellets swell and put a tensile hoop stress on the surrounding cladding, enlarging existing breaches[6-8] and, in some cases, creating new breaches.[7]

Spent fuel leaching and dissolution studies[9,10] are generally conducted with UO_2 pellets that are only a few years out of reactor and usually assume that the condition of a fuel pellet will not change prior to the ingress of ground water into the canister. For the 0.01% of the fuel rods that may enter the repository in a breached condition or the rods which breach while in the repository, the fuel phases and structural condition of breached rods will depend on the time of breach, temperature, atmosphere and, possibly, the radiation environment. Because the higher oxidation states of uranium may leach faster than UO_2, it is necessary to know to what extent they are present when leaching commences.

This paper will present preliminary results of thermogravimetric measurements which were conducted to obtain UO_2 oxidation rates between 200° and 225°C.

BACKGROUND

Tuff Repository Conditions After Canister Breach

According to 10CFR60,[3] "the engineered barrier system shall be designed . . . so that containment of HLW within the waste packages will be substantially complete for a period to be determined . . . such period shall be not less than 300 years nor more than 1000 years after permanent closure . . ." For this study we assume that the canister may breach and expose the fuel to water-saturated air sometime between 300 years and 1000 years after emplacement.

Since oxidation is a thermally-activated process, the temperature of the fuel is important. Based on a number of different canister emplacement configurations, Stein, et al.[11] determined that the maximum fuel centerline temperature should be 145° to 160°C after 300 years and less than 115°C at 1000 years. While the temperatures have not been calculated beyond 1000 years, it can be assumed the temperature will slowly decrease thereafter.

The time dependence of the gamma field intensity can be calculated assuming that the dose rate is approximately proportional to the quantity of fission products.[12,13] The gamma intensity will have dropped from 6×10^4 R/hr for ten-year-old fuel at the time of emplacement to ~70 R/hr after 300 years. By 1000 years after emplacement when canister breach might first be expected to occur, the gamma intensity will have dropped to ~4 R/hr. The neutron field should not be significant for oxidation considerations because it is many orders of magnitude higher in the reactor than in storage. Thus, all damage to the crystalline structure will have already taken place, and gamma decay will provide much more ionization than neutron emission. If ionization is an influencing factor, the gamma field will override the neutron field. The short ranged alpha flux due to actinide decay was not calculated but should decrease slowly with time.

Thermodynamic Considerations in the Oxidation of UO_2

The free energies of formation of the uranium oxides indicate that UO_2 is unstable with respect to oxidation to the higher oxides, U_3O_8 and UO_3, under the temperature and atmosphere conditions that spent fuel may experience in a tuff repository. Early studies indicated that, below 250°C, UO_2 oxidized only to U_3O_7 but this may have been due to the short duration of the tests which usually lasted for less than 30 days. In one study,[14] after storage in air for 15 years, weak x-ray diffraction lines of $UO_3 \cdot 2H_2O$ were found. The relationships among oxide phases that may form during oxidation are shown in the phase diagram[15,16] (see Fig. 1).

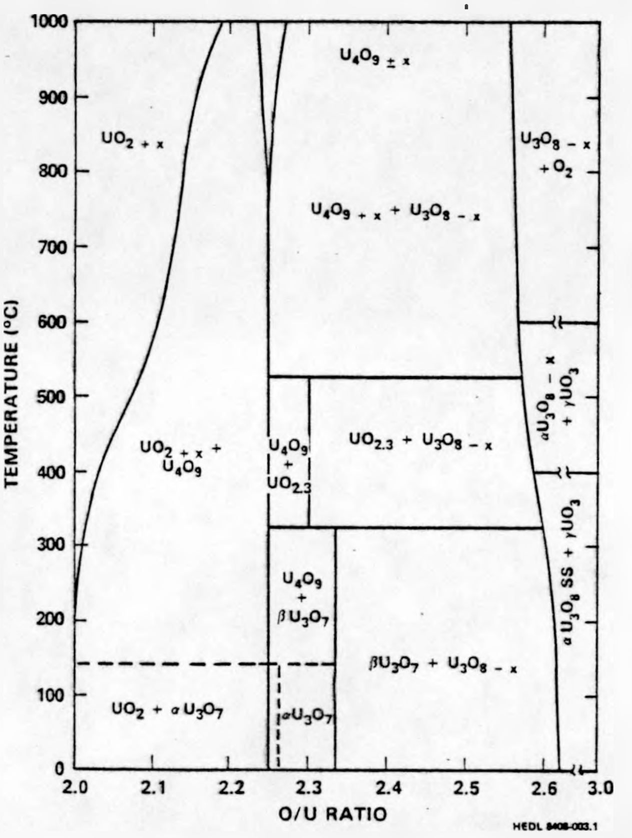

Fig. 1. Phase diagram for uranium-oxygen system adapted from References 15 and 16.

Equations (1) and (2) represent the formation of U_3O_8 from UO_2 and its subsequent oxidation to UO_3.

$$3\ UO_2 + O_2 = U_3O_8 \qquad (1)$$

$$2\ U_3O_8 + O_2 = 6\ UO_3 \qquad (2)$$

The standard free energy changes accompanying these two oxidation reactions are calculated by means of the equations

$$\Delta G_1^o = \Delta G_f^o\ (U_3O_8) - 3\Delta G_f^o(UO_2) \qquad (3)$$

$$\Delta G_2^o = 6\Delta G_f^o\ (UO_3) - 2\Delta G_f^o(U_3O_8) \qquad (4)$$

where the quantities, ΔG_f^o, represent the standard state free energies of formation of the uranium oxides indicated within the parentheses. The negative values for ΔG_1^o and ΔG_2^o given in TABLE I[17,18] for temperatures ranging from 25°C to 250°C demonstrate that the reactions may occur but disclose nothing about their rates. Equilibrium oxygen partial pressures corresponding to ΔG_1^o and ΔG_2^o may be obtained from the equation

$$\ln P_0 = \Delta G°/RT \qquad (5)$$

and range from 10^{-47} to 10^{-7} atmosphere for temperatures between 25° and 250°C. The presence of air in a tuff repository obviously would provide oxygen well in excess of these equilibrium pressures. Consequently, if the necessary activation energy is provided, reactions 1 and 2 will occur as written.

TABLE I

Free Energy Changes Accompanying the Oxidation of UO_2 and U_3O_8

	ΔG° (kcal/mol O_2)*	
T (°C)	UO_2 to I_3O_8	U_3O_8 to UO_3
25	-64.82	-26.96
100	-62.12	-23.54
150	-60.34	-21.28
200	-58.54	-19.00
250	-56.77	-16.72

*Evaluated using values for the free energy of formation of UO_3, U_3O_8, and UO_2 from References 17, 18.

Spent Fuel Oxidation Studies

Only two oxidation studies have been made on irradiated PWR fuel and none on BWR fuel. The majority of the work has been performed on unirradiated pellets, CANDU fuel or AGR fuel, and may not be applicable to LWR fuel. No experiments are known to have been done in a controlled-moisture atmosphere. Laboratory air with its contained moisture is ordinarily used.

Differences in the oxidation behavior of unirradiated and irradiated fuel can be due to at least two reasons. First, during irradiation, the UO_2 crystalline structure is damaged and pellets are fragmented, thus opening more surface area to oxidation. In addition, gas bubbles and fission products may migrate to the grain boundaries where interconnected paths can form, making grain boundaries preferential sites for oxidation. Secondly, the fission product and actinide decay creates a radiation field which can ionize or excite atmospheric oxygen, possibly enhancing the oxidation rate. The first effect would manifest itself as a function of the spent fuel burnup while the second effect is dependent on the radiation field present in the repository.

Two studies have been conducted which compare the behavior of irradiated and unirradiated fuel. White, et al.[19] compared the behavior of Point Beach spent fuel with that of UO_2 pellets fabricated in the laboratory. They found a large difference in the oxidation rate, which they attributed to enhancement by irradiation. However, the fuel came from two different sources and because fabrication characteristics such as grain size may affect oxidation, the results are not conclusive. Hastings and Novak[20,21] and Boase and Vandergraaf[22] compared the oxidation behavior before and after irradiation for fuel made for the Bruce reactor. In both studies, little or no enhancement of the oxidation rate due to irradiation was found. Below 250°C, it appears that there may be some enhancement of the oxidation rate due to irradiation but the enhancement is less than an order of magnitude. The data are not sufficient to determine if the rate is further enhanced at still lower temperatures. A study on the oxidation of breached segments of Turkey Point fuel rods showed considerably faster fuel oxidation on the segments taken near the end of the rod.[23] This has been tentatively attributed to the lower burnup near the rod end. The cause of this burnup effect has not yet been determined.

All of the recent lower temperature UO_2 oxidation studies have been concerned with dry storage or fuel handling. While some x-ray diffraction has been done, most of the phase formation information is inferred from weight change curves. Because the oxide density does not decrease until U_3O_8 is formed, most of the studies have been concerned with detecting U_3O_8. Time-to-spallation is the most commonly used measure, because it is an easy visual observation. These studies reveal little about the rate of formation of oxides other than U_3O_8. They do indicate, though, that oxidation rates are strongly affected by temperature.

Outstanding Questions

Based on the variability of spent fuel and the expected conditions in a tuff repository, additional data are needed to determine the low temperature spent fuel oxidation mechanisms and to evaluate the effects of spent fuel oxidation in a tuff repository at low temperatures. In particular, oxidation data and evaluations are needed to address the following concerns:

1. The mixture of uranium oxide phases as a function of time at repository temperatures is unknown and is needed for model evaluation.
2. There may be low activation energy or athermal processes which are dominant at repository temperatures but of little consequence at higher temperatures where the thermal reaction dominates. Such a case is illustrated in Fig. 2.
3. The effect of high repository humidity and fuel variability in the long-term, low-temperature oxidation mechanisms has not been determined.

EXPERIMENTAL PROCEDURE

Fuel Samples

PWR fuel from Turkey Point assembly B-17 was chosen since it is similar in properties and irradiation history to the ATM-101 H. B. Robinson fuel and was used in other oxidation tests at higher temperatures.[23] The fuel is representative of low fission gas release PWR fuel irradiated to near the present day peak burnup. Characteristics of the Turkey Point fuel are given in TABLE II. Many companion fuel rods from the same assembly have been extensively characterized, both destructively and nondestructively,[12,24] including gamma scanning, fission gas release, fuel grain size, fuel density and SEM examination, for example. The fuel for the present tests came from rods I9 and G7. After the rods were cut, the clad sections were stored in a sealed air atmosphere at room temperature for a number of years. The fuel removed from the cladding was fragmented, which is typical of irradiated UO_2. Due to radiation dose rate constraints in the TGA, the sample size was limited to approximately 200 mg or approximately one fragment. In one case, the fuel was further pulverized to determine surface area effects. The equivalent spherical diameter of the fuel fragments was ~0.4 cm while that of the pulverized fuel, which consisted of particles each containing several grains, was ~0.01 cm. The ratio of the total sample surface areas of the pulverized fuel to fragmented fuel was ~40.

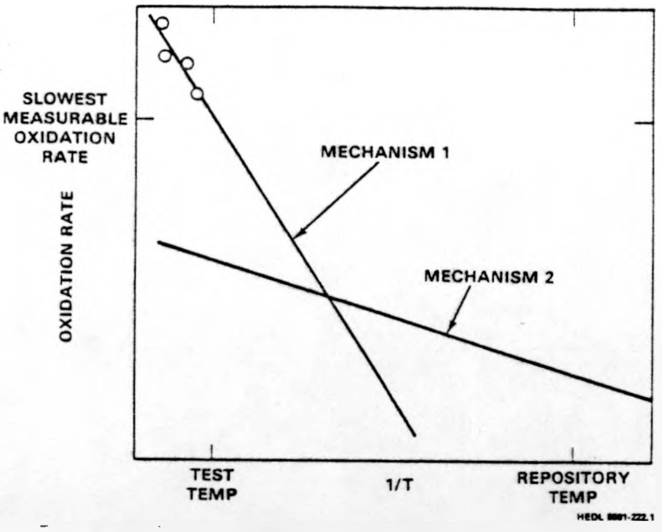

Fig. 2. Extrapolation of high temperature oxidation data with two operating mechanisms. Extrapolation using *high temperature measurements may be in* error at lower temperatures if a low activation energy process is also active.

TABLE II

Characteristics of Turkey Point Unit 3 Fuel

Characteristics	Turkey Point
Fuel Type	PWR 15 x 15
Assembly Identification	B-17
Discharge Date	November 25, 1975
Nominal Burnup	27 MWd/kgU
Fission Gas Release	.03%
Initial Enrichment	2.559 wt% ^{235}U
Initial Pellet Density	92% TD (UO_2)
Initial Rod Diameter	10.7 mm OD
Cladding Material	Zircaloy-4
Cladding Thickness	0.62 mm

The spent fuel is subjected only to its own radiation field generated by the fission products and actinides in the sample itself. 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 seen had it remained in the fuel assembly, but the gamma field in 10-year-old fuel is 800 to 15,000 greater than in 300 and 1000 year old fuel. Even the pulverized 10 year old fuel has a self gamma field which is over 40 times greater than that emitted by fuel in an assembly after 300 years. Therefore, no external fields are needed in low temperature oxidation testing.

Test Procedure

A TGA (thermogravimetric analysis) system consists of an analytical balance that continuously weighs the fuel specimen, which is heated to a constant temperature in a furnace and exposed to an atmosphere of fixed composition. The apparatus is suited for continuously measuring small changes in oxidation that are associated with a weight change.

A schematic of the WHC TGA system is shown in Fig. 3. The device is located in an unshielded glovebox, which precludes exposing the fuel sample to external fields. The furnace can be readily controlled to ±1°C. A weight change of 0.005%, equivalent to 10 μg is well within the accuracy and sensitivity of the microbalance. The moisture content of the atmosphere is controlled by a refrigeration unit down to a dew point of -70°C (2 ppm H_2O by volume). All dew points used in testing were maintained below room temperature to prevent condensation in the lines or balance.

The weighed sample was placed in the TGA system, which was then evacuated. Room air was admitted and recirculated at a flow rate of about 400 cc/min. The sample was brought to temperature in 30 minutes and was weighed continuously. After the desired oxidation period, the sample was removed and reweighed to confirm the total weight change. Because agreement with the weight change measured on a continuous basis was generally excellent, the absence of drift in the TGA system was demonstrated. After testing, the samples were examined by ceramography, x-ray diffraction and, in some cases, ion microprobe.

RESULTS AND DISCUSSION

Five samples have been tested by TGA in order to determine the stability of the equipment and to obtain preliminary indications of effects of the repository conditions and spent fuel variability on the oxidation rates. Tests were conducted in the temperature range from 200° to 225°C in order that meaningful results could be obtained in a relatively short period of time. X-ray diffraction, ion microprobe analysis and ceramography were conducted on some samples to obtain additional information on the oxide phases and possible oxidation mechanisms. The test conditions for each of the runs are given in TABLE III.

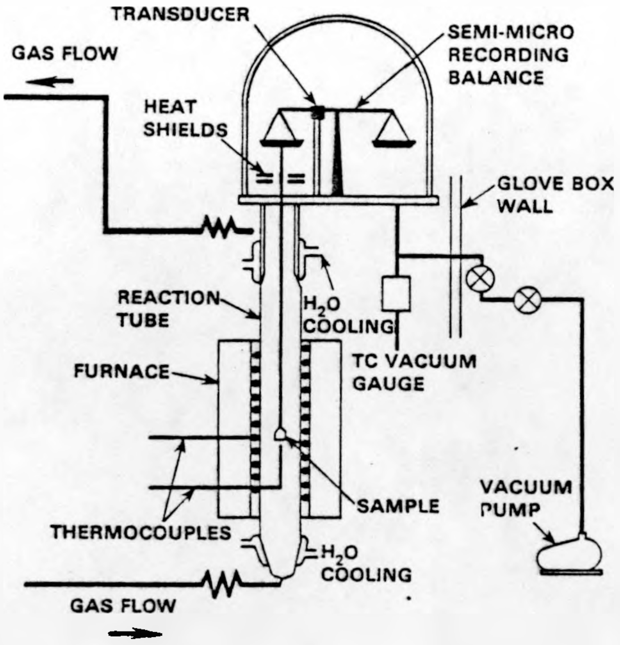

Fig. 3. Schematic of WHC TGA system used in low temperature oxidation testing.

The percent weight gain of the fuel specimen is plotted as a function of time in Fig. 4. Individual points, which were taken from recorder tracings, are shown on two of the curves to illustrate the minor amount of scatter. Two O/M (oxygen to metal ratio)

TABLE III

Test Parameters

	Test 1	Test 2	Test 3	Test 4	Test 5
Temperature (°C)	225	224	200	225	225
Duration (Hrs)	356	408	737	387	428
Atmosphere	Air	Air	$80\%N_2 + 20\%^{18}O_2$	Air	Air
Dew Point (°C)	14.5	14.5	14.5	-69.8	14.5
Fuel Identification*	G7-27-2	I9-24-1	I9-24-2	G7-14-3-1	G7-14-3-2
Initial Weight (mg)	195.2	228.5	227.6	214.6	211.5
Sample Condition	Pulverized Fuel	Single Fragment	Single Fragment	Two Fragments	Four Fragments

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* G7, I9 refer to the fuel rod identification

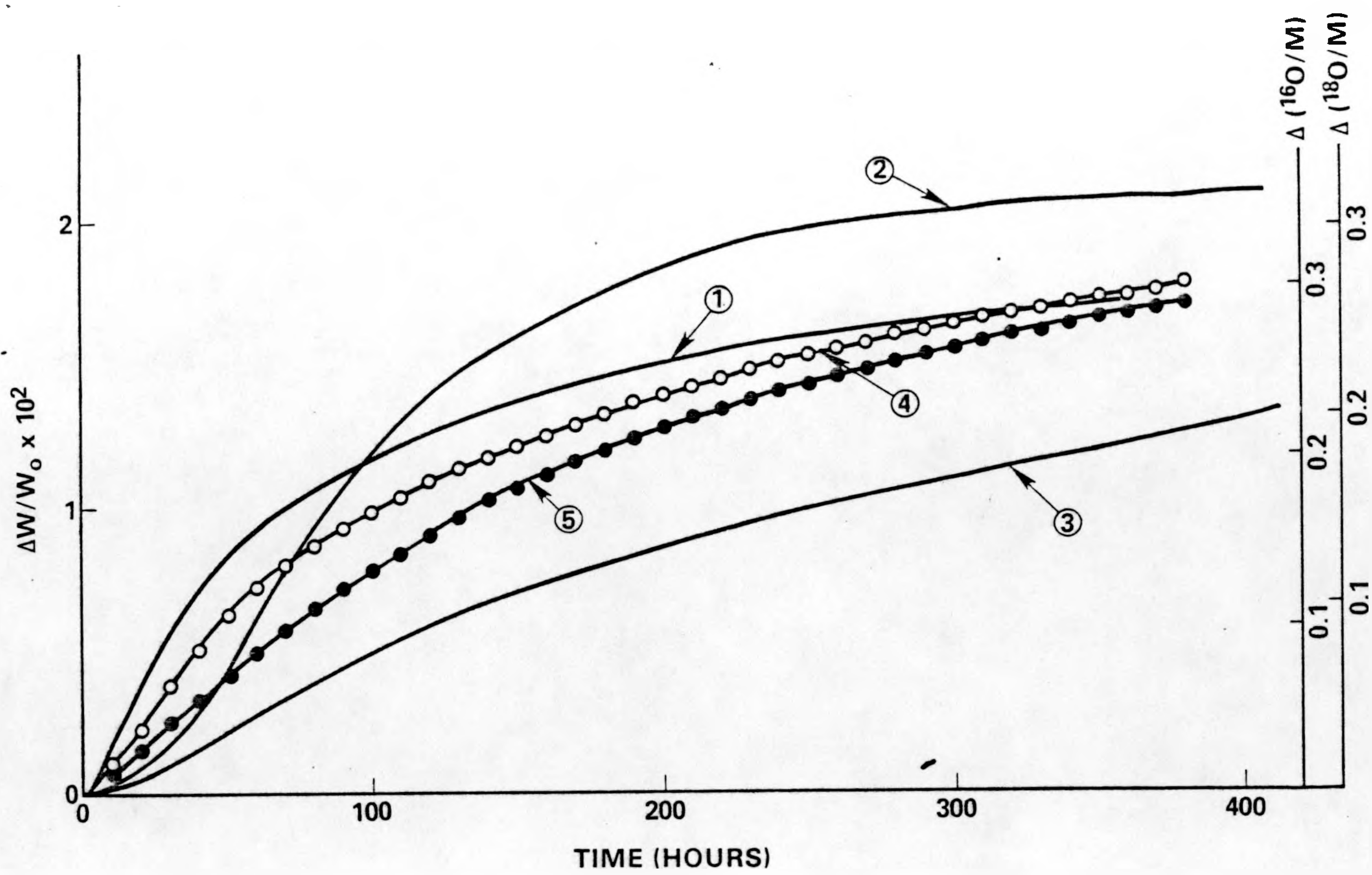

Fig. 4. TGA test sample weight changes. Conditions of each run are given in TABLE III. Circles are actual typical data.

scales are shown, since the weight change for the same change in O/M is 12.5% larger for oxidation with $^{18}O_2$ compared to $^{16}O_2$.

Particle Size Effect

If surface area controlled the rate of oxidation, then the rate of weight increase[20] during the initial stages of oxidation should have been proportional to the surface area. The pulverized fuel used in test 1 had a geometric surface area ~40 times larger than the fragments of fuel, but the rate of 2×10^{-2} %ΔW/hr for test 1 was only a factor of 2 to 3 larger than the rates of 1.1×10^{-2} and 7.6×10^{-3} measured in tests 4 and 5. It is difficult to compare tests 1 and 2 due to the shape of the weight gain curve in test 2, but even there the average weight gain over the first 100 hours is the same as in test 1.

Unetched ceramographic sections of both the pulverized (test 1) and fragmented fuel (test 2) taken at the conclusion of the test indicate significant grain boundary attack at the location of the polished surface, about 180 μm below the original sample surface (see Figs. 5 and 6). Grain boundaries usually cannot be seen optically in as-irradiated fuel unless etched. It appears that oxygen is rapidly penetrating the grain boundaries, an observation also supported by ion microprobe data. Test 3 used a mixture of 80% N_2 + 20% $^{18}O_2$ as the oxidant. After 737 hours, the fuel sample had an O/M ratio of 2.26. Thus, after correcting for the $^{18}O_2$ composition, the average $^{18}O_2/^{16}O_2$ ratio should be 0.10. The ratio was measured at two different arbitrarily selected interior locations of the fragment. The average ratio on the grain boundaries was 0.035 ± 0.017 while off the grain boundaries it was 0.012 ± 0.006; approximately a factor of three greater on the grain boundaries. While the amount of $^{18}O_2$ was less than expected, at least in the areas examined, the measurements do indicate that O_2 is penetrating the grain boundaries to the interior of the fragment.

Initially there appear to be two operative processes: 1) diffusion into and oxidation of the grain boundaries and 2) bulk oxidation of the grains. At the start of oxidation the total surface area of the pulverized fuel is available for oxidation essentially immediately. Because the external surface area of the fuel fragment is much smaller, the initial oxidation rate is slower until the more rapid grain boundary diffusion and oxidation open up the internal surface for oxidation. The larger apparent incubation period of oxidation in test 2 compared to tests 4 and 5 may be due to the initial inability of the oxygen to penetrate the grain boundaries. Eventually the rates of weight gain for the pulverized fuel and fragmented fuel approach the same value as bulk diffusion into the grains becomes rate controlling.

B. Diffusion and Temperature Effects

If it assumed that grain-boundary diffusion and oxidation are very fast when compared to diffusion and oxidation within individual grains, as indicated above, then the fuel specimen can be treated as an assembly of individual grains. Assuming also that the grains are spherical and that oxidation is controlled by oxygen diffusion through the layer of product formed

Fig. 5. As-polished cross-section of the pulverized fuel oxidized in +14.5°C dew point air at 225°C for 356 hours. Note the grain boundaries are usually seen only in etched UO_2 (250X).

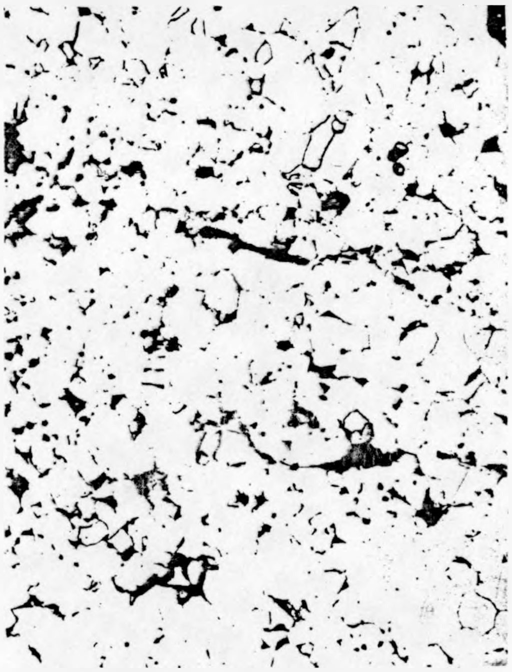

Fig. 6. As-polished cross-section approximately 180 μm deep into the fragment oxidized in 14.5°C dew point air. Note the grain boundaries are usually seen only in etched UO_2. (500X)

on the grain surface, the rate equation can be written

$$\frac{d(r_0 - r)}{dt} = \frac{k}{(r_0 - r)} \tag{6}$$

where r_0 = radius of the unoxidized grain
$r_0 - r$ = depth of oxidation = thickness of U_3O_7 layer
t = time
and k = rate constant.

If Eq. (6) is integrated, the depth of oxidation at any time is given by

$$r_0 - r = (2kt)^{1/2} \tag{7}$$

Neglecting the small density change, the extent of conversion of UO_2 to U_3O_7 is

$$C = 1 - \left(\frac{r}{r_0}\right)^3$$

or

$$r_0 - r = r_0 [1 - (1 - C)^{1/3}] \tag{8}$$

Equating Eqs. (7) and (8) and rearranging

$$[1 - (1 - C)^{1/3}] = \frac{1}{r_0} (2kt)^{1/2}$$

or, because r_0 is a constant for a given fuel,

$$[1 - (1 - C)^{1/3}] = (k't)^{1/2} \tag{9}$$

where $k' = 2k/r_0^2$.

If it is assumed that the diffusion-controlled stage of oxidation is represented by the reaction

$$3\ UO_2 + 1/2\ O_2 = U_3O_7$$

then the fractional conversion of UO_2 to U_3O_7 is given by

$$C = \frac{\Delta N_{UO_2}}{N^{\circ}_{UO_2}} = \frac{3\Delta W/16}{W^{\circ}_{UO_2}/270} = 3\Delta(O/M) \tag{10}$$

Thus, a plot of $[1 - (1 - 3\,\Delta O/m)^{1/3}]$ versus $t^{1/2}$ will be linear if the rate of oxidation is controlled by diffusion. Such a plot is shown in Fig. 7. The linearity of these plots following the initial period during which oxygen rapidly permeates and oxidizes the grain boundaries and then commences attacking the grains appears to indicate that diffusion through the product layer on the grain surface is controlling the oxidation rate. The rate constants obtained from the slopes of these lines may be found in TABLE IV.

Although results at only two temperatures can hardly be considered definitive, an activation energy was nevertheless calculated with the rate constants given in TABLE IV. The values obtained, 25.5 kcal/mol, agrees well with literature values,[25] which generally range from 20 to 30 kcal/mol.

C. Moisture Effect

The moisture level in test 4 (dew point ≅ -70°C) was ~3 ppm compared to a level of ~16,000 ppm in the other tests, over three orders of magnitude difference in moisture level. Tests 4 and 5 were identical except for the moisture levels. Comparison of the weight gain curves in Fig. 5 shows a somewhat slower rate in test 5 where the moisture concentration was higher. This may be due to a longer time for the oxygen to penetrate the grain boundaries (see TABLE IV), an

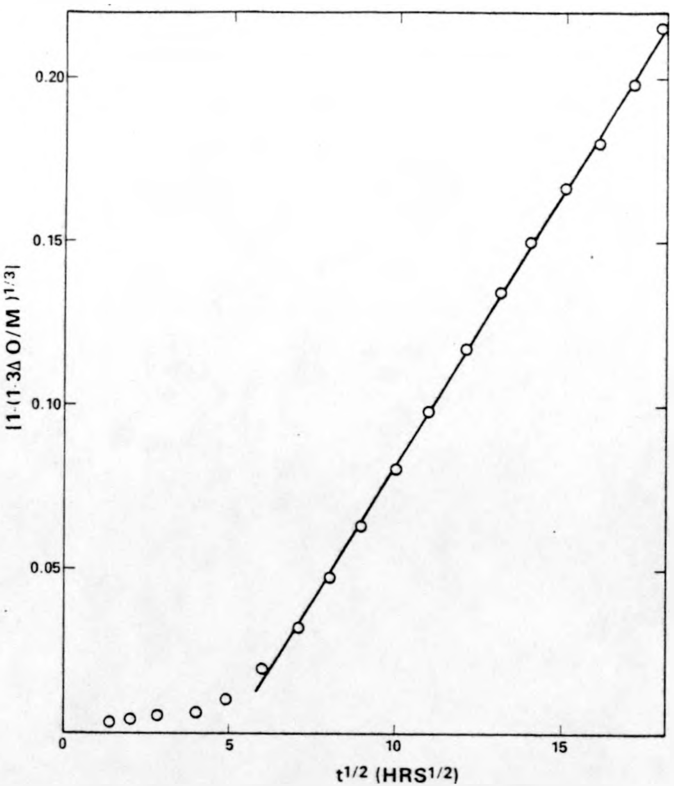

Fig. 7. Oxidation of spent Turkey Point PWR fuel in air at 225°C - test 4.

effect resulting from adsorption of water molecules, which do not cause oxidation, on grain boundary surfaces. After the rate is controlled by diffusion into the grains, the rate constant (k) is the same for both cases. A similar comparison could be made between tests 4 and 1, remembering that test 1 used pulverized fuel. Here, the weight gains are higher at the higher moisture level because grain boundary diffusion is not so critical. When the rates are controlled by diffusion into the grains, they are again the same in both cases. This seemingly ambiguous effect of moisture on the oxidation rate is in agreement with earlier studies carried out on unirradiated UO_2. The preliminary indication is that the effect of moisture on the oxidation rate is not great.

CONCLUSIONS

The present tests were conducted to determine if TGA is a suitable experimental technique for studying long-term oxidation and to obtain a preliminary indication of the important parameters affecting spent fuel oxidation. The conclusions based on the results of these tests are preliminary in nature. Considerable testing for longer times and at lower temperatures will have to be conducted before the spent fuel oxidation mechanisms are established and extrapolation of spent fuel oxidation behavior in a tuff repository can be made. The following preliminary conclusions are offered.

1) The TGA system appears to have sufficient stability to provide excellent oxidation data. The small samples appear to adequately represent the fuel being studied.

2) The size of the fuel samples does not appear to influence its long-term oxidation rates. It appears that grain boundary diffusion allows rapid access to the oxidizing atmosphere to most of the grains making up the fuel specimen. This rapidly increases the surface area available for bulk diffusion and oxidation.

3) Over a range of 3 ppm to 16,000 ppm of H_2O, the moisture content of the air has only a minor effect on the short-term oxidation rate, which may decrease with increasing moisture.

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TABLE IV

Results of Preliminary Oxidation Tests

Test #	1	2	3	4	5
Final O/M	2.29	2.35	2.26	2.30	2.30
Initial Rate of Weight Gain (%/hr)	2×10^{-2}	NM	5×10^{-3}	1.1×10^{-2}	7.6×10^{-3}
Approximate Time When Diffusion Control Starts (hrs)	8	64 (?)	36	20	64
k' (hr^{-1})	0.033	0.07	0.017	0.031	0.034
Temperature (°C)	225	224	200	225	225

NM - Not Measured

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