Pacific Northwest National Laboratory

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Oxidation Rate of K-Basin Spent Nuclear Fuel in Moist Air

J. Abrefah
H. C. Buchanan
S. C. Marschman

June 1998

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Experiments have been conducted by Pacific Northwest National Laboratory to determine the oxidation rate of damaged/corroded N-Reactor fuel material in moist air. These measurements were performed in support of the safety and process analyses of the proposed Integrated Process Strategy to move the N-Reactor fuel stored at the water-filled K-Basins to an interim dry storage facility. These limited experiments on the reactivity of K-Basin spent nuclear fuel (SNF) material in moist air were conducted using a thermogravimetric system and were part of the broad studies undertaken to ascertain the bounding oxidation rate of the SNF in various atmospheres, including dry air.

Five SNF pieces (with regular geometrical shapes) sectioned from a damaged element stored in the K-West Basin were oxidized in flowing air containing moisture. The partial pressure of the moisture in the gas stream was the same (i.e., 12.33 kPa) for all five tests, but the isothermal condition was varied between 198°C and 350°C. The results of the reactivity of the damaged/corroded SNF in moist air are compared to dry air oxidation of the SNF material and the theoretical prediction for unirradiated uranium in both dry and moist air.

The SNF oxidation behavior in moist air at a temperature of 198°C can best be fitted by parabolic oxidation kinetics. A linear rate equation gave the best fit to the oxidation data at 250°C and above. The results within the temperature range studied, therefore, show a transition from parabolic oxidation kinetics (i.e., protective oxide layer) to linear oxidation kinetics (i.e., cracking and spallation of the oxide layer). The transition temperature is somewhere between 198°C and 250°C.

The tests at approximately 300°C gave results that were very different from the other tests at temperatures of 198°C, 250°C, and 349°C. The SNF sample weight change at this temperature showed erratic behavior. Visual examination indicated the sample fragmented into small pieces and powder as a result of rapid oxidation and hydration. Additional tests at temperatures close to 300°C (i.e., 300±10°C) are recommended in order to fully understand the oxidation behavior of the damaged/corroded SNF samples in moist air at about 300°C.

In comparison with the oxidation kinetics of SNF material in dry air (Abrefah et al. 1998⁽¹⁾), there was no significant difference between the moist air oxidation rate and the dry air oxidation rate of the damaged/corroded SNF samples within the applicable temperature range. This observation is analogous to the conclusion of Pearce et al. (1988⁽²⁾), who observed no enhancement effect of moisture on oxidation kinetics of swollen (due to irradiation) uranium material.

(1) Abrefah J., H. C. Buchanan, W. M. Gerry, W. J. Gray, and S. C. Marschman. 1998. *Dry Air Oxidation Kinetics of K-Basin Spent Nuclear Fuel*. PNNL-11786, Pacific Northwest National Laboratory, Richland, Washington.

(2) Pearce R. J., M. J. Bennet, and J. B. Price. 1988. "Oxidation of Irradiated Uranium in Moist Air." *Nuclear Energy* 27(5):305.

Acknowledgments

The campaign to ship SNF samples from the K-West canisters to Pacific Northwest National Laboratory for characterization activities, including the oxidation tests, was made possible through the dedicated efforts of the operations staff at the K-Basins and the DE&S Hanford, Inc., SNF characterization group under the management of Ronald Omberg and his associates, Bruce Makenas, David Bergmann, and Leo Lawrence. The authors also thank the hot cell technicians of the Postirradiation Testing Laboratory and the Radiochemistry Processing Laboratory (Shielded Analytical Laboratory) who were involved in preparing the TGA test samples. Finally, we thank Sue Gano for her editorial work and John Latkovich for his efforts in getting this report cleared and published.

Quality Assurance

This work was conducted under the Quality Assurance Program, Pacific Northwest National Laboratory (PNNL) SNF-70-001, *SNF Quality Assurance Program*, as implemented by the PNNL *SNF Characterization Project Operations Manual*. This QA program has been evaluated and determined to effectively implement the requirements of DOE/RW-0333P, Office of Civilian Radioactive Waste Management (OCRWM) *Quality Assurance Requirements and Description (QARD)*. Compliance with the QARD is mandatory for projects that generate data used to support the development of a permanent High-Level Nuclear Waste repository. Further, the U.S. Department of Energy has determined the testing activities that generated the results documented in this report shall comply with the QARD.

Although the data used in this report were generated in compliance with the PNNL OCRWM-compliant QA program, those data are insufficient to develop fully defensible conclusions regarding the oxidation behavior of N-Reactor fuel material in moist atmospheres. Thus, some of the conclusions reached in this report are qualitative in nature. This is noted where appropriate.

Supporting records for the data in this report are located in the permanent PNNL SNF Characterization Project records, *Oxidation Rate of K-Basin Spent Nuclear Fuel in Moist Air*.

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Table

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Acronyms

DSC	differential scanning calorimeter
ID	identification
IPS	Integrated Process Strategy
KW	105-K West
MS	mass spectrometer
PNNL	Pacific Northwest National Laboratory
OCRWM	Office of Civilian Radioactive Waste Management
QA	Quality Assurance
QARD	Quality Assurance Requirements and Description
QMS	quadrupole mass spectrometer
SEM	scanning electron microscope
SNF	spent nuclear fuel
TGA	thermogravimetric analysis
UHP	ultra high purity

1.0 Introduction

During the processing of N-Reactor spent nuclear fuel (SNF) for interim dry storage on the Hanford Site, the proposed Integrated Process Strategy (IPS) (WHC 1995) will dry the SNF under atmospheric conditions ranging from pure water vapor to pure inert atmospheres. A testing program is in progress at Pacific Northwest National Laboratory (PNNL)^(a) to determine the oxidation kinetics of the SNF in different atmospheres representing the proposed IPS processes. This program consists of a series of tests, reported in separate documents. The test discussed here was conducted to determine the oxidation rate of fuel samples in moist air. Samples for testing were taken from the damaged/corroded region of an outer N-Reactor fuel element.

A review report on metallic uranium oxidation behavior in moist air (Pearce et al. 1988) concluded that the oxidation rate of irradiated, and hence swollen, uranium was independent of partial pressure of water vapor. However, because the oxidation behavior of damaged/corroded SNF material in dry air was shown to be different from unirradiated uranium in PNNL studies (Abrefah et al. 1998a), the possibility that moist air oxidation could also be different was considered. This report provides the results of experiments conducted on the SNF samples using a thermogravimetric system under isothermal conditions ranging from 198°C to 350°C and at a partial pressure of 12.33 kPa (93 Torr). The reactivity results are compared with the dry air oxidation results from the PNNL studies and the theoretical prediction for unirradiated uranium in both dry and moist air.

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2.0 Experimental Method

The moist air oxidation studies of damaged/corroded fuel samples were performed using a thermogravimetric system installed in the Radiochemical Processing Laboratory (325 Building). The test samples were sectioned from an outer N-Reactor fuel element that was shipped from the 105-KW Basin to the Postirradiation Testing Laboratory (327 Building) for both destructive and nondestructive examination. A brief discussion of the experimental system and the test samples is given in the sections below.

2.1 TGA/DSC/MS System

The testing was conducted using a Netzsch STA 409 TGA/DSC/MS (thermogravimetric analysis/differential scanning calorimeter/mass spectrometer) skimmer graphite furnace system. A schematic representation of the TGA/DSC/MS testing system is shown in Figure 2.1. The system is made up of four chambers: an MS chamber, an intermediate chamber, a sample reaction chamber, and a balance chamber. The MS chamber, which houses a quadrupole mass spectrometer (QMS), is pumped by a turbomolecular pump to a baseline vacuum pressure of about 10^{-7} Torr. The intermediate chamber separates the MS chamber from the atmospheric reaction chamber, and it is pumped by a mechanical pump to a baseline pressure of about 10^{-3} Torr without a load. The sample chamber houses a thermogravimetric sample carrier, which has the sample thermocouple (i.e., S-type). The sample carrier is connected to the analytical balance. Gas inlet and outlet lines are connected to this chamber to supply the reactant gas. The sample crucible, with dimensions of 15 mm outside diameter, 12 mm inside diameter, a depth of 7.2 mm, and a height of 9 mm, is mounted at the end of the sample carrier (Figure 2.1). The sample chamber is resistively heated by graphite elements that are protected by ultra high purity (UHP) helium gas flow through the element shell chamber. The analytical balance chamber houses the electrobalance and a gas inlet to the chamber that allows it to be purged by either an inert gas or the reactant gas. The temperature of the analytical chamber is maintained at ambient conditions by a series of heat shields in the sample chamber and a water cooling at the joint that separates this chamber from the heated sample chamber.

The water vapor was supplied to the system using a bubbler that was maintained at constant temperature. The flowing reactant air passed through the bubbler to pick up the water vapor fraction at a partial pressure given by the saturated water vapor pressure at the set temperature. The actual water vapor pressure was not monitored in the system.

2.2 Sample Preparation and Testing

The SNF samples used for the oxidation kinetics studies were taken from the damaged region of element SFEC5,4378 (Figure 2.2). The initial sectioning of the damaged element was done with a milling machine with a silicon carbide blade. The cutting surfaces were cooled by flowing argon through a vortex cooling tube (Chilcut-II). The sectioned pieces were stored in UHP argon to minimize further

Figure 2.1. Schematic of the TGA/DSC/MS System

Figure 2.2. Damaged End of SNF Element SFEC5,4378

degradation. A low-speed, precision cut-off saw (Buehler Isomet or LECO VC-50) with a diamond wafering blade was used to generate the small TGA testing samples. Each sample had four cut uranium surfaces and two surfaces with the bonded inner and outer cladding (Zircaloy-2). The weight and the dimensions of the samples were measured in the Shielded Analytical Laboratory hot cell (325 Building) prior to loading them into the TGA system for the test. The dimensions of the initial exposed uranium surfaces, shown in Figure 2.3, were used to calculate the initial geometric surface area listed in Table 3.1 (Section 3.2). The samples were used in the as-cut condition without polishing or removal of the native oxide film (formed by exposure of the cut uranium surfaces to air). Samples were free of any visible surface cracks or voids.

Figure 2.3. Sketch of Pre-Test TGA Sample and Dimensions

The samples were oxidized under flowing air containing about 12.33 kPa (93 Torr) of water vapor at a constant temperature and a system pressure of 1 atmosphere. The partial pressure of the water vapor in the reacting gas stream was determined from a saturation water vapor pressure table at a bubbler temperature of 50°C. Before each oxidation test, the sample chamber was purged with the moist air after loading the sample. The sample was then heated at a constant rate of 15°C/min to the desired temperature while flowing moist air at a rate of about 200 cm³/min through the sample chamber. The electrobalance chamber was kept inert by flowing UHP helium through it. The sample temperature was then maintained at isothermal conditions up to about 6 hr. This allowed sufficient time to collect data for oxidation rate analyses. The isothermal treatment was followed by cooling to ambient temperature. For the test at 349°C (TGA Run 15), the system was shut down before the scheduled period ended due to rapid oxidation of the sample. The sample weight change was continuously monitored by the electrobalance throughout the test, and the off-gas stream was analyzed by the attached QMS. Four different temperature tests were performed in the temperature range of about 198°C to 350°C.

3.0 Analytical Results and Discussion

3.1 Experimental Data

The oxidation behavior of the SNF samples at five isothermal conditions is shown in Figures 3.1 and 3.2. The weight change curve at 198°C for TGA Run 13 (Figure 3.1a) is characteristic of a parabolic oxidation kinetics. The initial time-dependent oxidation rate is higher than the linear oxidation rate at the latter part of the experiment. The time period for transition from a nonlinear rate to a linear rate at the sample temperature of 198°C is about 150 min, which agrees well with the data for the dry air oxidation at 200°C (Abrefah et al. 1998a). The results at 198°C thus indicate that a protective oxide film can be formed on the SNF at (and maybe below) 198°C in a moist air atmosphere.

Figure 3.1b shows the oxidation of SNF in moist air at 299°C. The weight change data are noisy and erratic. At the initial stage of the test, the plot indicates a weight loss by the sample, followed by a series of weight gains and losses. The post-test visual examination showed that most of the SNF sample oxidized and disintegrated (Figure 3.3 displays the sample photographs). Some of the oxidation products were shaped like whiskers. The dispersible particulates from the oxidation process were distributed throughout the system, which supports the sudden weight losses seen in the weight change curve (Figure 3.1b). For a heavily oxidized sample, the maximum weight gain of about 10 mg, measured in Figure 3.1b, is too low to account for the total oxygen pickup by the sample. From the visual examination of the post-test sample, it can be inferred that at least 10 wt% of the test sample was oxidized (initial weight of the sample was 6.61 g). For oxidation of about 10 wt% of the sample, the expected weight gain is about 90 mg (assuming UO_2 as the product), which is higher than the average 10 mg measured. Because of the significant difference between the expected and the measured weight change, the estimated oxidation rate for this run (TGA Run 14) is not an accurate rate for the SNF material and should not be used.

The oxidation of SNF in moist air at 349°C is illustrated in Figure 3.1c. The weight change data at this temperature follow a linear oxidation kinetics, which is an indication of nonprotective oxide scale formation. The oxide spallation for this test may have been more frequent during the oxidation process.

Figures 3.2a and 3.2b show the oxidation of SNF in moist air at 250°C and 300°C, respectively. The weight change data at 250°C best follow a linear oxidation behavior with slight deviation to a parabolic (i.e., small curvature of the plot) profile. The data for 300°C, Figure 3.2b, did not give any indication of weight gain, but the sample was almost consumed at the end of the run. The behavior in this run was a repeat of the behavior run for TGA Run 14 (Figure 3.1b) at somewhat lower temperature, but again the results failed to give useful weight gain data for oxidation rate determination. The weight change curve shows a sudden weight increase at the beginning of the test only, and, for most parts of the run, the weight change curve shows either weight loss (at the initial stages) or no appreciable weight change.

Figure 3.1. Plots of Weight Change Versus Time for Oxidation of SNF Sample in Moist Air at (a) 198°C for TGA Run 13, (b) 299°C for TGA Run 14, and (c) 349°C for TGA Run 15

Figure 3.2. Plots of Weight Change Versus Time for Oxidation of SNF Sample in Moist Air at
(a) 250°C for TGA Run 29 and (b) 300°C for TGA Run 30

Figure 3.3. Photographs of SNF Sample After Oxidation in Moist Air at 299°C. Top photograph shows the residue of the oxidation products on the heat shield plates of the TGA system; bottom photograph shows the oxidized and expanded sample in the crucible.

The results of TGA Run 14 at 299°C (Figure 3.1b) and TGA Run 30 at 300°C (Figure 3.2b) show that the SNF sample readily oxidized, disintegrated, and formed whiskers at around this temperature (Figure 3.3) in moist air. Comparing the photographs in Figure 3.3 with a scanning electron microscope (SEM) examination of sludge materials from the K-Basin (Abrefah et al. 1998b) and the SEM photomicrographs in the report of Taylor et al. (1989), it can be inferred that there may be small crystals of UO_3 hydrates formed during the test at 300°C. The thermal decomposition of the hydrates may explain the long period of weight loss observed during these two runs. The samples may have experienced both weight gain (oxidation and hydration reactions) and weight loss (thermal decomposition of the hydrates and particulates falling from the crucible). Consequently, the weight change data at this temperature look "noisy." The two results also indicate that the oxidation of uranium in moist air can be complicated by sequential reaction of the oxide film with water to produce hydrated oxides. The formation of hydrated oxides can produce a porous, nonprotective layer that can further expose the metal substrate to the oxidants (i.e., water and oxygen), which in turn may increase the reactivity of uranium in a moist air atmosphere.

3.2 Oxidation Rate

A general fit of the weight change curve at 198°C for TGA Run 13 with an equation of the form, $\Delta w = a + mt^n$, yielded a value for n of 0.5 (Figure 3.4), which supports the parabolic oxidation kinetics for SNF in moist air at that temperature. The data taken at temperatures 250°C and 349°C yielded a value of 1 for n , which indicates linear oxidation kinetics for those temperatures. The test results at 300°C for TGA Run 30 were not analyzed, but the data at 299°C for TGA Run 14 were fitted with an average linear rate.

The four linear oxidation rates of damaged SNF samples in moist air are listed in Table 3.1, and shown in Figures 3.5 and 3.6 are the linear regression fits to the weight change versus time curves. The oxidation rate for TGA Run 13 at 198°C is the best linear rate calculated from the weight gain versus time curve (Figure 3.5a). The oxidation rate data for SNF in air with water vapor partial pressure of about 12 kPa are plotted in Figure 3.7, excluding the measurements in TGA Run 14. A linear regression line is drawn through the three experimental data points to estimate the temperature-dependent rate constant. This yields a rate constant of

$$k = 1.67 \times 10^5 \exp(-67/RT) \text{ mg/cm}^2/\text{min}$$

where the activation energy is kJ/mol, R is the gas constant, and T is the absolute temperature. This equation is given for comparison only. Because of the very limited amount of data available, this rate equation should not be used as an accurate representation of the oxidation kinetics of damaged SNF in moist air.

Figure 3.4. A Fit of the Weight Change Versus Time Curve with Equation, $y = a + bx^n$. The solid line represents the best fit with $a = -2.781$, $b = 0.985$ and $n = 0.5$ for TGA Run 13

Table 3.1. Oxidation Rate of SNF Sample in Moist Air

TGA Run	Sample Characteristics			Test Temperature (°C)	Regression Results		Oxidation Rate (mg/cm ² /min)
	ID	Weight (g)	Surface Area (cm ²)		Slope (mg/min)	r ²	
13	5-S1A-E2C	7.53	2.88	198	0.0320	1.00	0.0111
14	5-S1A-E2D	6.61	2.79	299	0.016 ^(a)	0.72	0.0057
15	5-S1A-E3D	4.27	2.15	349	1.304	1.00	0.6065
29	5-S1A-E2B	7.46	2.78	250	0.100	1.00	0.0360
30	5-S1A-E3E	5.10	2.39	300	N/A ^(a)	--	--
ID = identification							
(a) Erratic weight gain versus time curve.							

In Figure 3.8, the moist air oxidation rate measurements are compared to the dry air oxidation rate equation (solid line) of SNF material (Abrefah et al. 1998a). Within the experimental spread of the data, there is no significant difference between the moist air oxidation kinetics and the dry air oxidation kinetics of the damaged/corroded SNF samples. This observation is analogous to the conclusion of Pearce et al. (1988) on the effect of moisture on oxidation kinetics of swollen (due to irradiation) uranium material. They concluded that there was no enhancement effect of moisture on the oxidation rate. The independence of the oxidation rate of damaged/corroded SNF material in air containing water vapor might be due to two characteristics of the SNF material, the distribution of hydride in the sample matrix and the presence of microcracks. These characteristics can affect the reactive surface area and the formation of a protective oxide film on the surface of the uranium. The spallation of these oxide layers, with the corresponding increased reactive area, can increase the linear oxidation kinetics of SNF material in either moist or dry air atmospheres. Additionally, direct oxidation of hydride inclusions in the damaged SNF sample can increase its effective oxidation rate in either moist or dry air such that any enhancement effect due to the added moisture to the air becomes negligible.

The oxidation rate published in the literature (Pearce et al. 1988) for unirradiated, metallic uranium oxidation in dry air and in moist air are plotted in Figure 3.9, together with the current moist air SNF data in Figure 3.9 for comparison. The solid and dotted lines in Figure 3.9 correspond to the moist air oxidation rate and dry air oxidation rate of Pearce et al. (1988), respectively. Within the spread of the SNF oxidation data, the Pearce et al. moist air oxidation rate equation may more closely bound the SNF moist air oxidation data than it does dry air at lower temperatures.

Figure 3.5. Linear Regression Fit to the Weight Change Data for Oxidation of SNF Sample in Moist Air at (a) 198°C for TGA Run 13 and (b) 299°C for TGA Run 14

Figure 3.6. Linear Regression Fit to the Weight Change Data for Oxidation of SNF Sample in Moist Air at (a) 250°C for TGA Run 29 and (b) 349°C for TGA Run 15

Figure 3.7. Arrhenius Plot of SNF Oxidation Rate in Moist Air

Figure 3.8. Comparison of SNF Oxidation Rate in Moist Air with the Rate Equation for SNF in Dry Air (Abrefah et al. 1998a)

Figure 3.9. Comparison of Oxidation Rates of Damaged SNF Material in Air Containing About 12 kPa Water Vapor Partial Pressure and the Calculated Values of Pearce et al. (1988) for Unirradiated Uranium Oxidation Rate Equation (6) for Moist Air and Equation (4) for Dry Air

4.0 Conclusions

The three oxidation rates of the damaged/corroded SNF material in air containing 12.33 kPa water vapor partial pressure were not significantly different from the dry air oxidation rate (Abrefah et al. 1998a). This observed behavior suggests that the oxidation rate of the damaged/corroded SNF uranium may not be affected by the presence of moisture in air.

The three oxidation rates for the damaged/corroded SNF also fall slightly below the theoretical prediction using Equation (6) of Pearce et al. (1988) developed for the moist air oxidation rate of unirradiated metallic uranium. Thus, the limited data have shown that the oxidation rate of damaged/corroded SNF material in moist air may be bounded by the theoretical equation of Pearce et al. (1988) for unirradiated uranium in moist air. Additional data for the SNF material in moist air at the same partial pressure and different pressures are necessary for these observations to be valid.

The SNF oxidation behavior in moist air at a temperature of 198°C can best be fitted by parabolic oxidation kinetics. However, a linear rate equation gave the best fit to oxidation data at temperatures above 250°C. The results within the temperature range studied, therefore, show a transition from parabolic oxidation kinetics (i.e., protective oxide layer) to linear oxidation kinetics (i.e., cracking and spallation of the oxide layer). The transition temperature is between 198°C and 250°C.

The tests at approximately 300°C gave results that were very different from the other tests at temperatures of 198°C, 250°C, and 349°C. The SNF sample weight change at 300°C showed erratic behavior. Visual examination after the test indicated fragmentation of the sample and formation of whisker-like oxidation products. Additional tests at temperatures close to 300°C (i.e., 300±10°C) are recommended in order to fully understand the observed oxidation behavior of the damaged SNF sample.

5.0 References

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