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REACTION RATE CONSTANT FOR DRY AIR OXIDATION OF K BASIN FUEL

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Abstract: The rate of oxidation of spent nuclear fuel stored in the K Basin water is an important parameter when assessing the processes and accident scenarios for preparing the fuel for dry storage. The literature provides data and rate laws for the oxidation of unirradiated uranium in various environments. Measurement data for the dry air oxidation of K Basin fuel is compared to the literature data for linear oxidation in dry air. Equations for the correlations and statistical bounds to the K Basin fuel data and the literature data are selected for predicting nominal and bounding rates for the dry air oxidation of the K Basin fuel. These rate equations are intended for use in the Spent Nuclear Fuel Project Technical Databook.

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Description: Reaction rate constant for dry air oxidation of K Basin fuel for process and safety calculations.

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REACTION RATE CONSTANT FOR DRY AIR OXIDATION OF K BASIN FUEL

1.0 PURPOSE

The purpose of the calculations outlined here is to update the equations for the reaction rate constant for dry air oxidation of the irradiated N Reactor fuel that has been stored in the K Basins (K Basin fuel). The equations herein are submitted for reference in the Project Technical Databook (Duncan 1997) to be used for both process and safety base calculations. Reaction rate constants are necessary input parameters for calculation of the reaction of K Basin fuel metal in Multi-Canister Overpacks (MCOs) with a number of different atmospheres. The reaction rate constants in this Project Technical Databook submittal are the best estimates based on the available data. The equations will be updated when sufficient additional data or an expanded understanding of materials behavior are available to warrant a revision.

2.0 SUMMARY STATEMENT OF PARAMETER

The reaction rate constant is defined in the following general equation.

$$R = A_s \times F_a \times k$$

where:

R = Reaction rate

A_s = Geometric fuel surface area

F_a = Enhancement factor to account for the following: (1) true reacting surface sometimes called a roughness factor, (2) alloy inclusions including hydrides, and (3) characteristics of the native oxide present on the reacting surface

k = Temperature dependent reaction rate, typically an Arrhenius form.

For Process Calculations

$$\text{Log } k = 4.451 - 2177/T \text{ for } T \leq 568 \text{ K}$$

$$\text{Log } k = 7.188 - 3732/T \text{ for } 568 < T \leq 695 \text{ K}$$

and

$$\text{Log } k = 3.857 - 1416/T \text{ for } T > 695 \text{ K}$$

where:

k is weight gain in $\text{mg}/\text{cm}^2/\text{hr}$ and T is temperature in degrees Kelvin (K).

Dry air is defined by less than 15 vppm H_2O .

Upper Bound for Safety Basis

$$\text{Log } k = 5.499 - 2177/T \text{ for } T \leq 655 \text{ K}$$

and

$$\text{Log } k = 4.338 - 1416/T \text{ for } T > 655 \text{ K}$$

Lower Bound for Safety Basis

$$\text{Log } k = 8.946 - 4638/T \text{ for } T \leq 352 \text{ K}$$

$$\text{Log } k = 6.370 - 3732/T \text{ for } 352 < T \leq 773 \text{ K}$$

and

$$\text{Log } k = 3.377 - 1416/T \text{ for } T > 773 \text{ K}$$

Enhancement Factor F_a

The enhancement factor F_a for dry air oxidation is defined to be

$$F_a = 1$$

Sample Calculation of Reaction Rate

For process calculations in a MCO a temperature of 75 °C was selected for the reaction rate for K Basin fuel oxidation in dry air.

The geometric surface area of an MCO for process calculations is defined to be (Duncan 1997)

$$A_s = 3 \times 10^3 \text{ cm}^2$$

for these calculations.

Therefore:

$$\begin{aligned} R &= A_s \times F_a \times k \\ &= (3 \times 10^3 \text{ cm}^2) \times (1) \times (10^{4.451-2177/348}) \\ &= (3 \times 10^3 \text{ cm}^2) \times (1) \times (0.0157 \text{ mg}/\text{cm}^2/\text{hr}) \\ &= 47.0 \text{ mg of weight gain/hour.} \end{aligned}$$

Oxidation of Clean Surfaces

A two-step linear model for the oxidation of relatively clean uranium surfaces in dry air is provided in Appendix D.

3.0 ASSUMPTIONS

The rate constants, k , recommended are for linear oxidation according to the following equation:

$$W = k \times t \quad (3.1)$$

where:

W is weight gain and t is time.

The initial oxidation of clean, unoxidized uranium surfaces in dry air occurs in a non-linear manner which has been modeled by Pearce and Kay (1987), Colmenares (1984) and Ritchie (1984) using a parabolic equation:

$$W = k \times t^{1/2} \quad (3.2)$$

With time an oxide layer develops on the surface and the rate decreases, progressing toward a linear rate. A parabolic equation has been used by Pearce and Kay (1987) and Colmenares (1984) to describe long-term oxidation in dry air. This equation has the form

$$W = k_p \times t^{1/2} + k_l \times t \quad (3.3)$$

where:

k_p and k_l are the parabolic and linear rate constants, respectively.

It is assumed that exposure of the fuel to the K Basin water has resulted in significant oxidation of the uranium surfaces and that only linear oxidation will be observed in dry air. This assumes that the non-linear component of the oxidation of clean surfaces will be insignificant due to the oxide buildup from long-time water exposure. Oxidation will therefore be linear and progress according to Equation (3.1).

4.0 SOURCES OF INFORMATION

Literature data for linear oxidation of unirradiated uranium in dry air were extracted from Figures 5 and 6 of Pearce (1989). These data, listed in Appendix A, were used in this document to derive a rate law for unirradiated uranium.

Supplemental data for dry air oxidation of uranium fuel was obtained from the French in an unpublished work by Paidassi et al. (1979) and from Bennett et al. (1975). These data, listed in Appendix B, include results from testing unirradiated and irradiated fuel materials.

Dry air oxidation data for damaged/corroded K Basin fuel was obtained from Abrefah et al. (1998). Appendix C lists the data used by Abrefah to derive a rate law for oxidation of K Basin SNF at temperature below 275 °C.

5.0 REACTION RATES

The issue is the number of corrosion events that occur in a given time at a given temperature. This is the product of the reactive fuel surface area and the corresponding rate constant. In actual practice it may not be necessary to know each of these two parameters if measurements of reaction products such as hydrogen are conducted. However, for modeling calculations specific values for each of these parameters are necessary. A fuel surface area recommendation was prepared and submitted by Lawrence (1998) for use in the Project Technical Databook (Duncan 1997). The reaction rate equations recommended here for inclusion in the Project Databook are consistent with the terms defined and used in the Databook.

5.1 DEFINITION OF TERMS

The primary interest in estimating oxidation rates of K Basin fuel in an MCO originates with the need to define the rate of potential chemical reactions. These reactions are exothermic and can result in the net production of gaseous products. Therefore, the reaction rates become important factors for predicting thermal transients in an MCO and the potential for over pressurization.

The reaction of uranium metal fuel in an MCO with a number of different reactants will occur as an MCO is loaded at the basins, transferred, dried, staged, conditioned, and stored. The reactants of interest can vary with the type of analysis under consideration (e.g., prediction of routine processing, analysis of accident conditions, etc.), however, the main reactants of interest include water, oxygen, and hydrogen. The general form of the relationship used to predict reaction rates is as follows.

$$R = A_s \times F_a \times k$$

where:

R = Uranium reaction rate, mg of weight gain/hr

A_s = Geometric surface area of uranium exposed to reactants, cm^2

F_a = Reactivity factor, to account for the true reacting surface sometimes called a roughness factor, dimensionless

k = Reaction rate constant, mg of weight gain/hr- cm^2

These terms are defined in more detail as follows.

Reaction Rate (R)--The reaction rate describes the mass of oxygen reacted per unit of time.

Geometric Surface Area (A_s)--The area of uranium exposed to reactants estimated by geometric dimensions assuming a smooth surface.

Reactivity Factor F_a --This enhancement factor accounts for the following: (1) the true reacting surface which can conceptually be thought of as the roughness of the actual uranium metal surface, increasing the smooth surface area associated with the geometric dimensions, (2) alloy inclusions including hydride, and (3) characteristics of the native oxide present on the reacting surface.

Temperature Dependent Rate Constant (k)--The reaction rate constant is typically an exponential function of inverse absolute temperature (Arrhenius relationship).

Reaction rate data are typically generated in the laboratory under controlled conditions and, for solid/gas or solid/liquid reactions, reported as a function of reactant concentration, temperature, and surface area. Placing the reaction rate data on a unit surface area basis allows use of the laboratory data for a variety of different configurations that may be encountered in practice. Specimens used to obtain laboratory data have some undefined degree of surface roughness which is ignored in this recommendation for dry air rate constant. Laboratory observations typically focus on determining the reaction rate dependence on temperature and reactant concentration.

5.2 AIR OXIDATION OF URANIUM

The chemical reaction for which the reaction rate constant will be used is:

Values for x range from $x \leq 0.25$ (Colmenares 1984) to $0.2 < x < 0.4$ (Orman 1976; Ritchie 1981) for temperatures up to 200 °C in dry air. At temperatures greater than 275 °C U_3O_8 starts to form (Orman et al. 1969).

Dry air is defined by less than 15 vppm H_2O .

5.3 LITERATURE DATA BASE FOR ANALYSIS

The reaction rate data base for dry air oxidation is a collection of linear rate data for unirradiated uranium from a large number of authors. The data base is shown in Figure 1 and tabulated in Appendix A. The Pearce equations previously selected by Cooper (1997) for the Technical Databook submittal was a correlation of linear rate data from the work of Pearce and Kay (1987) and recommended in Pearce (1989). These equations were compared to the literature data in Pearce (1989) and were not a correlation of these data.

5.4 REGRESSION ANALYSIS OF LITERATURE DATA

The literature data base (Appendix A) for unirradiated uranium expressed as the natural logarithm versus one over the absolute temperatures, i.e., $1/T$, was fit to linear equations over two and three different temperature intervals. An examination of the fits to the data lead to the selection of two temperature ranges where the regression analysis fixed the temperature where the two curves intersected. The data was also fit to a second order equation, i.e., $\log k = a + bT^2 + c/T$ with good statistics, i.e., $R^2 = 0.95$ however, this equation form was not selected since reaction rate data is normally expressed as a linear equation. The resulting equations are:

$$\log k = 7.188 - 3732/T \text{ for temperatures } \leq 695 \text{ K (422 } ^\circ\text{C)}$$

and

$$\log k = 3.857 - 1416/T \text{ for temperatures } > 695 \text{ K}$$

where:

k is the weight gain in $mg/cm^2/hr$ and T is temperature in K.

Dry air is defined by less than 15 vppm H_2O .

The corresponding upper bound 95% prediction interval lines for the data are approximated by:

$$\log k = 8.011 - 3732/T \text{ for temperature } \leq 631 \text{ K (358 } ^\circ\text{C)}$$

and

$$\log k = 4.338 - 1416/T \text{ for temperature } > 631 \text{ K.}$$

Figure 1. Data Base for Oxidation Rate of Uranium in Dry Air.
(Data presented represents sample weight gain.)

The corresponding lower bound 95% prediction interval lines for the data are approximated by:

$$\text{Log } k = 6.370 - 3732/T \text{ for temperatures } \leq 773 \text{ K (500 } ^\circ\text{C)}$$

and

$$\text{Log } k = 3.377 - 1416/T \text{ for temperatures } > 773 \text{ K}$$

The upper and lower 95% prediction interval lines from the regression analysis fixed the temperatures where the lines intersect resulting in different temperature limits for the upper and lower bound equations.

The two nominal equations and the upper and lower prediction equations for the data are compared to the data base in Figure 1. The upper and lower bounds adequately bracket the data and do not unduly compensate for the data scatter at any temperature or at the upper and lower ranges of the data. The goodness of the data fit is $R^2 = 0.93$ for the lower temperature range and $R^2 = 0.61$ for the higher temperature ranges.

The regression equation determined from the data can be used to predict a value for k at a given temperature, T . To insure that this prediction reflects the variability of the data used, a prediction interval was calculated at a given level of confidence. The 95% level was selected for the prediction interval, that is, 95% of the variability of the data for values of k predicted by the appropriate equation fall within the prediction interval.

The Pearce equations for dry air oxidation are as follows (Pearce 1989):

$$\text{Log } k = 8.9464 - 4638.2/T \text{ for } T < 597 \text{ K} \quad (5.1)$$

$$\text{Log } k = 28.381 - 7 \text{ Log } (T) - 4638.2/T \text{ for } T > 597 \text{ K} \quad (5.2)$$

These equations, presented in Revision 1 of the Technical Databook, are compared to the literature data base for unirradiated uranium in Figure 2.

5.5 COMPARISON TO FRENCH AND ENGLISH URANIUM DATA

Experimental work has been carried out in France and England in the late 60's and 70's (Paidassi et al. 1979; Bennett et al. 1975) in order to assess the behavior of uranium in dry and wet air. The uranium alloys used for this experimental work were Sicral FI for the French and the so-called adjusted uranium for the English measurements.

5.5.1 Comparison to Unirradiated Uranium Data

Available French data for unirradiated uranium were compared to the literature data and the regression analysis in Figure 3(a). This evaluation shows these data to be within the data scatter and will be adequately represented by the equations selected. The French data are listed in Appendix B.

Figure 2. Comparison of the Pearce Equations and the Regression Analysis of the Literature Data for Oxidation of Uranium in Dry Air.

Figure 3. Comparison of Regression Analysis for Dry Air Oxidation of Uranium with French and English Data for (a) Unirradiated Uranium and (b) Irradiated Uranium.

5.5.2 Comparison to Irradiated Uranium Data

Limited French and English data available for irradiated uranium was compared to the literature data regression analysis in Figure 3(b). The irradiated data were divided into two groups, corresponding to the fuel with less than 12% irradiation induced swelling and fuel with more than 12% swelling (Appendix B).

Comparing the unirradiated literature data and the irradiated (low swelling) data shows no significant influence of low swelling irradiation on the oxidation of uranium [Figure 3(b)].

On the other hand, some of the high swelling fuels data are outside the regression analysis for the literature data which is consistent with current understanding of the influence of swelling on oxidation rates. Voids and porosity are created in the fuels with high exposure resulting in higher fuel swelling. This additional porosity increases greatly the effective fuel surface area available for oxidation and correspondingly a higher measured oxidation rate.

The N Reactor fuel stored in the K Basins represents relatively low exposure fuel with low fuel swelling. Fuel burnup in the K Basins is mostly in the 11% to 15% ^{240}Pu range (Praga and Willis 1998) which translates to average fuel-column exposures of 2200 to 3900 megawatt days per metric ton uranium (MWD/MTU). Due to the typical N Reactor fuel column characteristics individual fuel element exposure can be 50% greater than the fuel-column average. This results in maximum fuel element exposures of 6000 MWD/MTU. Maximum fuel swelling of 3.5 vol% was measured in N-Fuel irradiated to 3100 MWD/MTU (Goffard and Last 1964). Using the model proposed by Goffard and Last, N-Fuel exposed to 6000 MWD/MTU will swell about 7.5 vol%. Therefore, the expected swelling of K Basin fuel due to reactor exposure is below the threshold for increasing the oxidation rate.

5.6 COMPARISON TO K BASIN FUEL DATA

Oxidation rates in dry air were measured for selected samples from the damaged portions of N Reactor fuel elements that were stored in the K West Basin (Abrefah et al. 1998). The laboratory measurements of K Basin spent nuclear fuel (SNF) are based on sample weight gain measured on the Thermo-Gravimetric Analysis (TGA) System and exposed geometric surface area measured from the samples' cut surfaces. These surfaces were visually free of cracks and surface voids. The measured rate data is an average of approximate linear portions of the samples weight gain versus time data plots for given sample temperatures. Two separate and independent analyses were performed using the TGA measurement data (Abrefah et al. 1998; Trimble and Welsh 1998).

5.6.1 K Basin Fuel Data Analysis

Seventeen samples from damaged/corroded portions of K Basin fuel elements were tested in dry air at temperatures ranging from 69 °C to 400 °C. Seven of these tests, at temperatures from 69 °C to 275 °C, exhibited normal oxidation behavior producing typical weight-gain curves (Abrefah et al. 1998). The

results from eight tests were atypical, and two additional tests used anomalous samples. Abrefah derived linear reaction rate constants for each of the seven normal test curves using regressions of the linear portion of each data curve that followed the initial parabolic portion of the test. This procedure is the normally accepted method for determining linear rate constants from reaction data and was used in deriving the linear rates reported in the literature (Table A1). The K Basin SNF data used by Abrefah are summarized in Appendix C and plotted on Figure 4(a).

The SNF data were fitted to an equation of the same form as used for the literature data. The nominal regression line, the 95% confidence interval on the mean, and the bounds on the 95% prediction interval are shown on Figure 4(a). The 95% confidence interval on the mean is the bounds on the certainty of the true mean of all SNF data, where the data set plotted on Figure 4(a) represents a sample of all SNF data. (There is a 5% probability that the mean reaction rate at a given temperature falls outside the 95% confidence interval). The 95% prediction interval is the predicted bounds for 95% of all data in the complete data set, where the complete data set represents all SNF surfaces in the K Basins. The nominal equation is

$$\text{Log } k = 4.451 - 2177/T.$$

The 95% prediction interval lines are approximated by the following equations:

Upper bound

$$\text{Log } k = 5.499 - 2177/T$$

Lower bound

$$\text{Log } k = 3.402 - 2177/T.$$

The K Basin SNF test data were also analyzed by Trimble and Welsh (1998). This analysis looked at the data from sixteen of the seventeen tests. The test run not evaluated (Run 21 at 300 °C) used an anomalous fuel material sample (Abrefah et al. 1998). All positive slopes in the data were used to derive a time-average rate constant for each test. The resulting sixteen data at 69 °C to 400 °C were evaluated on an Arrhenius plot. Statistical analysis found two of the rate constants to be probable outlier data relative to the remaining fourteen data. Regression of the fourteen data produced the following rate law equation:

$$\text{Log } k = 3.459 - 1802/T.$$

These data, the regression line, the 95% prediction interval lines and the lines for the 95% confidence interval on the mean are plotted on Figure 4(b).

The confidence interval on the mean from the two SNF data sets, (Abrefah et al. 1998; Trimble and Welsh 1998), are compared on Figure 4(c). The confidence intervals overlap substantially indicating that no significant difference exists between the two equations. Since the Abrefah data represents the normally accepted method for determining linear rate constant, the Abrefah rate law for K Basin SNF was used in the following discussions to derive rate law equations recommended by this document.

Figure 4. K Basin Fuel Dry Air Oxidation Data and Analysis.
 (a) Analysis by Abrefah et al., (1998) (b) Analysis by Trimble and Welsh (1998) (c) Comparison of Analysis Results.

The SNF data are compared on Figure 5 to the regression lines and the 95% prediction intervals to the data for unirradiated uranium (literature) data. The slopes of the two rate law equations were statistically analyzed for equality and were determined to not be equal. The SNF equation has less temperature dependence than does the literature data equation with the lines crossing at 295 °C. At and above 200 °C the SNF data falls within the bounds of the literature data but are above those bounds below about 150 °C.

5.6.2 Uncertainty in Spent Nuclear Fuel Data

The SNF samples tested for oxidation rate data were derived from two fuel elements from the closed canisters in K West Basin. The elements were damaged and corroded and the samples were from locations near the damage. These elements were intended to represent damaged fuel in the K West Basin. There are approximately 105,000 fuel assemblies (210,000 inner and outer elements) stored in the K East and K West Basins (Praga and Willis 1998). An estimated 70,000 of these elements are damaged exposing an estimated 1,000,000 cm² of uranium surface (Lawrence 1998). If corroded material causes accelerated corrosion, then measured oxidation rates from the tested samples would be expected to be representative of the oxidation rates for the total population of exposed fuel surfaces. However, because of the very large population of fuel in the Basins which have been irradiated and stored over a 10 to 30 year time frame, and because of the large variability in damaged and corrosion of these elements, there could be a significantly large variability in the material and its properties. Considering this and the very small sample size (two elements tested out of 70,000 damaged), the element-to-element variability has not been evaluated. Thus, there could be considerably more variability than observed by these SNF tests with some of that untested variability on the positive side of the oxidation rates. Caution should therefore be exercised in using these data.

5.7 RECOMMENDED REACTION RATE EQUATIONS

The recommended dry air reaction rate equations for the surfaces of K Basin SNF is based on the equations for damaged/corroded SNF at low temperature ($T \leq 568$ K) and on the literature data equations for unirradiated uranium at higher temperature. The temperatures at which the various nominal regression lines meet and at which the upper bounds meet and the lower bounds meet, define the break points for the recommended nominal, upper bound, and lower bound equations. The upper and lower bound equations are approximations to the 95% prediction interval lines. The bounds selected were the extremes available from the various prediction equations, except that the nominal Pearce Equation (5.1) was used where it fell below the lower bound for the literature data at $T = 352$ K.

For Process Calculations

$$\text{Log } k = 4.451 - 2177/T \text{ for } T \leq 568 \text{ K}$$

$$\text{Log } k = 7.188 - 3732/T \text{ for } 568 < T \leq 695 \text{ K}$$

$$\text{Log } k = 3.857 - 1416/T \text{ for } T > 695 \text{ K}$$

Figure 5. Comparison of Data Base and Regression Analysis for Dry Air Oxidation of Uranium with K Basin Fuel Data. (Data presented represents sample weight gain.)

Upper Bound for Safety Basis

$$\text{Log } k = 5.499 - 2177/T \text{ for } T \leq 655 \text{ K}$$

and

$$\text{Log } k = 4.338 - 1416/T \text{ for } T > 655 \text{ K}$$

Lower Bound for Safety Basis

$$\text{Log } k = 8.946 - 4638/T \text{ for } T \leq 352 \text{ K}$$

$$\text{Log } k = 6.370 - 3732/T \text{ for } 352 < T \leq 773 \text{ K}$$

and

$$\text{Log } k = 3.377 - 1416/T \text{ for } T > 773 \text{ K}$$

Where:

k is rate of weight gain in $\text{mg}/\text{cm}^2/\text{hr}$ and T is temperature in degrees Kelvin.

The recommended dry air reaction rate equations are represented graphically on Figure 6.

5.8 ENHANCEMENT FACTOR

The rate constant temperature dependence observed for the K Basin SNF is significantly different from that for unirradiated uranium literature data (Figure 5) or for the Pearce equation for dry air oxidation. This is also true for other dry air oxidation rate law equations found in the literature (Colmenares 1984; McGillivray 1994; Ritchie 1981). Because of this difference in rate law slope it is not practical to assign an enhancement factor to an existing equation to describe the oxidation of K Basin SNF. Thus, the reaction rate enhancement is embodied in the recommended rate law equations for K Basin SNF and in the upper bounds to those equations, and the enhancement factor, F_a , is assigned a value of one.

5.9 OXIDATION OF CLEAN SURFACES

The reaction rate equations presented in Section 5.7 are for linear oxidation of K Basin fuel. As previously discussed (Section 3), relatively clean surfaces will initially oxidize at a parabolic or non-linear rate. Such oxidation was observed in the testing of SNF at temperatures below 200 °C. Since this time dependent rate of oxidation can be substantial, a two-step linear oxidation rate was developed and is presented in Appendix D. If needed the equations in Appendix D can be used to evaluate the oxidation of relatively clean surfaces of K Basin SNF in dry air. Previously unexposed fuel surfaces created by fuel breakage during washing prior to MCO loading is an example of what could be relatively clean surfaces.

Figure 6. Graphical Representation of the Recommended Reaction Rate Equations for K Basin Fuel in Dry Air.

6.0 REFERENCES

- 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.
- Bennett, M. J., B. L. Myatt, D. R. U. Silvester, and J. E. Antill, 1975, "The Oxidation Behavior of Uranium in Air at 50-300 °C," *Journal of Nuclear Materials*, Vol. 57, pp. 221-236.
- Colmenares, C. A., 1984, "Oxidation of Mechanisms and Catalytic Properties of the Actinides," *Progress in Solid State Chemistry*, Vol. 15, pp. 257-364.
- Cooper, T. D., 1997, *SNF Project Recommended Reaction Rate Constants for Corrosion of N Reactor Fuel*, HNF-SD-SNF-TI-020, Rev. 1, B&W Hanford Company, Richland, Washington.
- Duncan, D. R., 1997, *Spent Nuclear Fuel Project Technical Databook*, HNF-SD-SNF-TI-015, Rev. 2, Duke Engineering & Services Hanford, Inc., Richland, Washington.
- Goffard, J. W. and G. A. Last, 1964, *Swelling Behavior of N Reactor Fuel Elements*, HW-79646, General Electric Hanford Atomic Products Operations, Richland, Washington.
- Lawrence, L. A., 1998, *Fuel Surface Area*, HNF-SD-SNF-CN-017, Rev. 1, Duke Engineering & Services Hanford, Inc., Richland, Washington.
- McGillivray, G. W., D. A. Geeson, and R. C. Greenwood, 1994, "Studies of the Kinetics and Mechanism of the Oxidation of Uranium by Dry and Moist Air," *Journal of Nuclear Materials*, Vol. 208, pp. 81-97, North Holland.
- Orman, S., 1976 "Oxidation of Uranium and Uranium Alloys," *Physical Metallurgy of Uranium Alloys*, Ed. J. J. Burke, Brook Hill Publishing Company.
- Orman, S., G. Picton, and J. C. Ruckman, 1969, *Journal of Oxidation of Metals*, Vol. 1, (1969) p. 199.
- Paidassi, J. R. Dominget, and J. Dixmier, 1979, *Comportement en presence d'air ou d'eau de l'uranium et de combustibles metalliques a base d'uranium irradie ou non*, CEA-SECMLG-11079, Unpublished Work, Atomic Energy Commission, Paris, France.
- Pearce, R. J., 1989, *A Review of the Rates of Reaction of Unirradiated Uranium in Gaseous Atmospheres*, RD/B/6231/R86, Central Electric Generating Board, Berkeley Nuclear Laboratories, United Kingdom.
- Pearce, R. J., and P. Kay, 1987, *The Reaction of Uranium in the U-O₂-H₂O and U-H₂O Systems*, TPRD/B/0954/R87, Central Electric Generating Board, Berkeley Nuclear Laboratories, United Kingdom.

6.0 REFERENCES (Continued)

- Praga, A. N., and W. L. Willis, 1998, *105-K Basin Material Design Basis Feed Description for Spent Nuclear Fuel Project Facilities*, HNF-SD-SNF-TI-009, Rev. 1, Duke Engineering & Services Hanford, Inc., Richland, Washington.
- Ritchie, A. G., 1984, "The Kinetics of the Initial Stages of the Reaction of Uranium with Oxygen," *Journal of the Less-Common Metals*, Vol. 98, pp. 193-214.
- Ritchie, A. G., 1981, "A Review of the Rates of Reaction of Uranium with Oxygen and Water Vapor at Temperatures Up to 300 °C," *Journal of Nuclear Material*, Vol. 102, pp. 170-182.
- Trimble, D. J., and T. L. Welsh, 1998, *Statistical Analysis of Oxidation Rates for K Basin Fuel in Dry Air*, HNF-SD-SNF-CN-035, Rev. 1, Duke Engineering & Services Hanford, Inc., Richland, Washington.
- Waber, J. T., 1952, *A Review of the Corrosion of Uranium and Its Alloys*, LA-1524, Los Alamos National Laboratory, Los Alamos, New Mexico.

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APPENDIX A

DATA BASE FOR DRY AIR OXIDATION OF UNIRRADIATED URANIUM

The data for dry air oxidation of unirradiated uranium is listed in Tables A1 and A2 (Pearce 1989). The tables consider the temperature ranges for the regression analysis. Table A1 includes the data and results of the regression analysis for temperatures below 694 K whereas Table A2 includes the data and results for temperatures greater than 694 K. The tables also include the results of the regression analysis for the upper and lower 95% prediction intervals.

References

- Pearce, R. J., 1989, *A Review of the Rates of Reaction of Unirradiated Uranium in Gaseous Atmosphere Report*, RD/B/6231/R86, Central Electric Generating Board, Berkeley Nuclear Laboratories, United Kingdom.
- Waber, J. T., 1952, *A Review of the Corrosion of Uranium and Its Alloys*, LA-1524, Los Alamos National Laboratory, Los Alamos, New Mexico.

Table A1. Data for Dry Air Oxidation of Unirradiated Uranium for Temperatures ≤ 441 °C. (Continued)

Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Oxidation Rate* (mg/cm ² /hr)	Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Oxidation Rate* (mg/cm ² /hr)
1	441	1.40	1.020e+02	26	320	1.68	7.000e+00
2	398	1.49	2.000e+01	27	310	1.71	1.400e+01
3	398	1.49	3.000e+01	28	308	1.72	4.800e+00
4	398	1.49	3.200e+01	29	305	1.73	1.200e+01
5	398	1.49	4.000e+01	30	305	1.73	2.000e+00
6	398	1.49	1.000e+02	31	300	1.75	4.000e+00
7	394	1.50	5.000e+01	32	300	1.75	5.000e+00
8	394	1.50	5.800e+01	33	300	1.75	2.500e+00
9	394	1.50	3.800e+01	34	300	1.75	3.000e+00
10	389	1.51	2.500e+01	35	300	1.75	4.500e+00
11	389	1.51	8.000e+01	36	295	1.76	4.300e+00
12	389	1.51	3.300e+01	37	295	1.76	1.000e+01
13	389	1.51	1.000e+02	38	295	1.76	5.000e+00
14	389	1.51	6.000e+01	39	295	1.76	3.200e+00
15	385	1.52	1.300e+01	40	290	1.78	2.100e+00
16	372	1.55	1.600e+01	41	290	1.78	1.600e+00
17	360	1.58	5.000e+01	42	290	1.78	4.500e+00
18	360	1.58	8.000e+01	43	290	1.78	2.500e+00
19	360	1.58	1.600e+01	44	283	1.80	2.200e+00
20	384	1.61	9.000e+00	45	274	1.83	9.000e+00
21	344	1.62	6.500e+00	46	270	1.84	1.600e+00
22	344	1.62	6.000e+01	47	268	1.85	1.300e+00
23	330	1.66	4.000e+00	48	268	1.85	6.500e+00
24	330	1.66	8.000e+00	49	268	1.85	1.600e+00
25	325	1.67	2.500e+01	50	268	1.85	5.000e-01

*Notation 1.020e + 02 = 1.020×10^2 .

Table A1. Data for Dry Air Oxidation of Unirradiated Uranium for Temperatures $\leq 441^\circ\text{C}$. (Continued)

Data Point	Temperature ($^\circ\text{C}$)	$10^3/T$ (K^{-1})	Oxidation Rate* ($\text{mg}/\text{cm}^2/\text{hr}$)	Data Point	Temperature ($^\circ\text{C}$)	$10^3/T$ (K^{-1})	Oxidation Rate* ($\text{mg}/\text{cm}^2/\text{hr}$)
51	262	1.87	1.800e+00	76	212	2.06	1.400e-01
52	260	1.88	1.050e+00	77	208	2.08	5.000e-01
53	260	1.88	1.400e+00	78	203	2.10	7.100e-01
54	260	1.88	1.600e+00	79	203	2.10	9.000e-02
55	254	1.90	8.000e-01	80	203	2.10	6.500e-02
56	254	1.90	1.000e+00	81	203	2.10	5.000e-02
57	254	1.90	4.000e-01	82	203	2.10	2.500e-02
58	254	1.90	1.400e+00	83	203	2.10	4.000e-01
59	250	1.91	1.050e+00	84	200	2.11	1.600e+00
60	250	1.91	1.600e+00	85	200	2.11	6.300e-02
61	250	1.91	1.900e+00	86	200	2.11	1.300e-01
62	245	1.93	8.000e-01	87	200	2.11	1.000e+00
63	237	1.96	6.500e-01	88	200	2.11	1.000e-01
64	237	1.96	1.050e+00	89	200	2.11	2.500e+00
65	235	1.97	3.500e-01	90	200	2.11	3.100e-01
66	230	1.99	1.300e+00	91	200	2.11	2.100e-01
67	230	1.99	4.500e-01	92	200	2.11	2.300e-01
68	227	2.00	6.500e-01	93	200	2.11	2.900e-01
69	227	2.00	5.000e-01	94	200	2.11	4.000e+00
70	227	2.00	8.000e-01	95	200	2.11	1.600e-01
71	227	2.00	4.000e-01	96	200	2.11	2.500e-01
72	227	2.00	1.600e-01	97	200	2.11	1.500e-01
73	227	2.00	9.000e-02	98	200	2.11	4.800e-01
74	225	2.01	8.000e-01	99	200	2.11	2.000e-01
75	220	2.03	5.000e-01	100	200	2.11	4.900e-01

*Notation $1.020\text{e} + 02 \equiv 1.020 \times 10^2$.

Table A1. Data for Dry Air Oxidation of Unirradiated Uranium for Temperatures ≤ 441 °C. (Continued)

Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Oxidation Rate* (mg/cm ² /hr)	Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Oxidation Rate* (mg/cm ² /hr)
101	199	2.12	5.000e-02	126	150	2.36	6.000e-03
102	199	2.12	2.000e-01	127	150	2.36	1.200e-02
103	199	2.12	1.000e-01	128	150	2.36	1.600e-02
104	199	2.12	2.500e-01	129	150	2.36	1.900e-02
105	197	2.13	1.100e+00	130	150	2.36	3.200e-01
106	192	2.15	7.000e-01	131	150	2.36	5.800e-03
107	192	2.15	1.000e+00	132	150	2.36	2.500e-02
108	192	2.15	4.000e-02	133	150	2.36	3.000e-02
109	188	2.17	1.600e-01	134	150	2.36	5.000e-02
110	188	2.17	1.000e-01	135	150	2.36	6.000e-02
111	182	2.20	4.000e-02	136	150	2.36	9.000e-02
112	180	2.21	4.500e-02	137	137	2.44	5.000e-03
113	180	2.21	1.600e-02	138	125	2.51	1.400e-02
114	180	2.21	1.500e-01	139	125	2.51	8.000e-03
115	180	2.21	5.000e-01	140	122	2.53	1.600e-03
116	180	2.21	1.000e-01	141	104	2.65	3.500e-04
117	180	2.21	5.000e-02	142	100	2.68	1.600e-04
118	170	2.26	4.000e-02	143	100	2.68	7.000e-04
119	170	2.26	1.000e-01	144	100	2.68	8.000e-04
120	170	2.26	5.000e-02	145	100	2.68	1.500e-03
121	167	2.27	1.000e-01	146	100	2.68	5.000e-03
122	160	2.31	3.300e-02	147	100	2.68	3.500e-03
123	160	2.31	1.600e-02	148	100	2.68	3.000e-03
124	158	2.32	1.300e-02	149	100	2.68	2.500e-03
125	150	2.36	2.000e-02	150	100	2.68	1.800e-03

*Notation 1.020e + 02 = 1.020×10^2 .

Table A1. Data for Dry Air Oxidation of Unirradiated Uranium for Temperatures ≤ 441 °C. (Continued)

Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Oxidation Rate* (mg/cm ² /hr)	Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Oxidation Rate* (mg/cm ² /hr)
151	96	2.71	6.600e-03	157	50	3.10	3.100e-05
152	74	2.88	1.000e-05	158	40	3.20	1.600e-05
153	72	2.90	1.250e-03	159	40	3.20	3.000e-05
154	60	3.00	3.200e-05	160	40	3.20	2.000e-05
155	60	3.00	1.000e-04	161 ¹	38	3.24	5.000e-05
156	60	3.00	1.500e-04				

¹This data point was changed from Pearce (1989) using correct value from the referenced source (Waber 1952).

*Notation 1.020e + 02 = 1.020×10^2 .

Table A2. Data for Dry Air Oxidation of Unirradiated Uranium for Temperature >441 °C. (Continued)

Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Oxidation Rate* (mg/cm ² /hr)	Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Oxidation Rate* (mg/cm ² /hr)
1	1420	0.59	1.500e+03	26	977	0.80	1.400e+03
2	1420	0.59	8.000e+02	27	977	0.80	1.600e+02
3	1420	0.59	1.800e+03	28	930	0.83	4.000e+02
4	1394	0.60	2.000e+03	29	930	0.83	6.700e+02
5	1200	0.68	6.000e+02	30	930	0.83	1.100e+02
6	1200	0.68	5.500e+02	31	930	0.83	5.000e+02
7	1200	0.68	5.000e+02	32	930	0.83	2.800e+02
8	1200	0.68	1.050e+03	33	930	0.83	8.000e+02
9	1200	0.68	8.000e+02	34	875	0.87	2.500e+02
10	1116	0.72	1.070e+03	35	825	0.91	6.000e+02
11	1116	0.72	1.600e+03	36	825	0.91	6.500e+02
12	1108	0.74	1.050e+03	37	814	0.92	2.000e+02
13	1025	0.77	1.400e+03	38	814	0.92	2.050e+02
14	1010	0.78	6.500e+02	39	800	0.93	4.000e+02
15	1010	0.78	2.500e+02	40	800	0.93	5.500e+02
16	1010	0.78	5.000e+02	41	780	0.95	6.300e+02
17	1010	0.78	4.500e+02	42	780	0.95	2.800e+02
18	1010	0.78	1.600e+02	43	780	0.95	2.900e+02
19	1010	0.78	1.700e+02	44	780	0.95	5.000e+02
20	1010	0.78	1.000e+03	45	780	0.95	3.300e+02
21	1010	0.78	9.500e+02	46	780	0.95	2.000e+02
22	1010	0.78	9.000e+02	47	780	0.95	3.400e+02
23	1010	0.78	8.000e+02	48	770	0.96	2.000e+02
24	1010	0.78	2.000e+02	49	760	0.97	2.500e+02
25	1010	0.78	6.700e+02	50	760	0.97	8.000e+02

*Notation 1.020e + 02 $\equiv$ 1.020 $\times$ 10².

Table A2. Data for Dry Air Oxidation of Unirradiated Uranium for Temperature >441 °C. (Continued)

Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Oxidation Rate* (mg/cm ² /hr)	Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Oxidation Rate* (mg/cm ² /hr)
51	760	0.97	1.800e+02	76	630	1.11	1.000e+03
52	760	0.97	1.900e+02	77	630	1.11	2.000e+02
53	727	1.00	3.800e+02	78	630	1.11	1.300e+02
54	710	1.02	2.200e+02	79	630	1.11	4.500e+02
55	710	1.02	3.800e+02	80	620	1.12	3.200e+02
56	710	1.02	2.000e+02	81	620	1.12	1.800e+02
57	710	1.02	1.900e+02	82	620	1.12	2.600e+02
58	700	1.03	8.000e+01	83	620	1.12	1.600e+02
59	700	1.03	5.000e+02	84	610	1.13	1.490e+02
60	660	1.07	2.000e+02	85	610	1.13	1.850e+02
61	650	1.08	3.000e+02	86	610	1.13	1.150e+02
62	650	1.08	1.600e+02	87	610	1.13	1.050e+02
63	650	1.08	2.500e+02	88	610	1.13	1.610e+02
64	650	1.08	1.050e+02	89	610	1.13	1.730e+02
65	645	1.09	5.000e+02	90	610	1.13	1.950e+02
66	645	1.09	3.500e+02	91	610	1.13	1.370e+02
67	645	1.09	4.000e+02	92	610	1.13	2.000e+02
68	645	1.09	2.100e+02	93	600	1.15	2.100e+02
69	645	1.09	1.050e+02	94	600	1.15	1.600e+02
70	645	1.09	2.000e+02	95	600	1.15	1.800e+02
71	640	1.10	1.800e+02	96	600	1.15	1.650e+02
72	640	1.10	4.000e+02	97	575	1.18	9.500e+01
73	640	1.10	2.000e+02	98	575	1.18	2.000e+02
74	640	1.10	3.500e+02	99	575	1.18	8.000e+01
75	640	1.10	2.100e+02	100	565	1.19	7.000e+01

*Notation 1.020e + 02 = 1.020 x 10².

Table A2. Data for Dry Air Oxidation of Unirradiated Uranium for Temperature >441 °C. (Continued)

Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Oxidation Rate* (mg/cm ² /hr)	Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Oxidation Rate* (mg/cm ² /hr)
101	560	1.20	9.500e+01	119	495	1.30	5.500e+01
102	560	1.20	8.000e+01	120	495	1.30	6.500e+01
103	560	1.20	1.050e+02	121	495	1.30	6.700e+01
104	560	1.20	1.400e+02	122	495	1.30	1.800e+02
105	560	1.20	2.000e+02	123	495	1.30	9.000e+02
106	560	1.20	2.500e+02	124	490	1.31	8.000e+01
107	545	1.22	9.500e+01	125	490	1.31	9.000e+01
108	545	1.22	6.000e+01	126	490	1.31	1.050e+02
109	535	1.24	2.500e+02	127	490	1.31	1.000e+02
110	535	1.24	1.030e+02	128	480	1.33	1.000e+02
111	510	1.28	1.100e+02	129	450	1.38	5.000e+01
112	510	1.28	8.000e+01	130	450	1.38	1.300e+02
113	500	1.29	2.000e+02	131	450	1.38	1.400e+02
114	500	1.29	9.000e+01	132	450	1.38	6.000e+01
115	500	1.29	1.000e+02	133	445	1.39	1.400e+02
116	500	1.29	6.500e+01	134	445	1.39	1.050e+02
117	495	1.30	6.000e+01	135	445	1.39	5.000e+01
118	495	1.30	8.000e+01				

*Notation 1.020e + 02 $\equiv$ 1.020 x 10².

APPENDIX B

SUPPLEMENTAL FRENCH AND ENGLISH DATA FOR DRY AIR OXIDATION OF URANIUM

Supplemental data for dry air oxidation of unirradiated uranium from the French and English is listed in Table B1 (Bennett et al. 1975; Paidassi et al. 1979). Limited data on the behavior of irradiated uranium is listed in Table B2.

References

- Bennett, M. J., B. L. Myatt, D. R. U. Silvester, and J. E. Antill, 1975, "The Oxidation Behavior of Uranium in Air at 50-300 °C," *Journal of Nuclear Materials*, Vol. 57, pp. 221-236.
- Paidassi, J. R. Dominget, and J. Dixmier, 1979, *Comportement en presence d'air ou d'eau de l'uranium et de combustibles metalliques a base d'uranium irradie ou non*, CEA-SECMLG-11079, Unpublished Work, Atomic Energy Commission, Paris, France.

Table B1. Supplemental French Data for Dry Air
Oxidation of Unirradiated Uranium.

Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Rate (mg/cm ² /hr)	Reference
1	100	2.68	5.2×10^{-3}	Paidassi 1979
2	150	2.36	1.1×10^{-2}	Paidassi 1979
3	200	2.11	0.59	Paidassi 1979
4	200	2.11	0.30	Paidassi 1979
5	200	2.11	0.19	Paidassi 1979
6	200	2.11	0.16	Paidassi 1979
7	250	1.91	0.48	Paidassi 1979
8	300	1.75	3.08	Paidassi 1979
9	300	1.75	2.29	Paidassi 1979
10	300	1.75	2.78	Paidassi 1979
11	400	1.49	151.00	Paidassi 1979
12	500	1.29	151.70	Paidassi 1979

Table B2. Supplemental French and English Data on
Oxidation of Irradiated Uranium in Dry Air.

Data Point	Temperature (°C)	$10^3/T$ (K ⁻¹)	Rate (mg/cm ² /hr)	Reference
Less than 12% Fuel Swelling				
1	150	2.36	4.90×10^{-3}	Paidassi 1979
2	200	2.11	0.43	Paidassi 1979
Greater than 12% Fuel Swelling				
1	100	2.68	2.80×10^{-3}	Bennett 1975
2	200	2.11	1.13	Paidassi 1979
3	200	2.11	0.87	Paidassi 1979
4	200	2.11	1.12	Paidassi 1979
5	250	1.91	4.80	Paidassi 1979
6	300	1.75	231.70	Paidassi 1979
7	300	1.75	128.70	Paidassi 1979
8	300	1.75	146.80	Paidassi 1979
9	400	1.49	131.60	Paidassi 1979
10	500	1.29	143.90	Paidassi 1979
11	500	1.29	102.30	Paidassi 1979

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APPENDIX C

K BASIN FUEL DATA FOR DRY AIR OXIDATION

The laboratory measurements of oxidation of K Basin fuel material in dry air are summarized in Table C1 (Abrefah et al., 1998).

References

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.

Table C1. Oxidation Rate of K Basin Spent Nuclear Fuel in Dry Air.

TGA Run	Sample Number	Sample Weight (g)	Test Temperature (°C)	Sample Geometric Surface Area (cm ²)	Oxidation Rate (mg/cm ² /hr)
51	10-S3-A2	6.02	69	2.41	0.0278
49a	10-S3-A3	6.03	90	2.41	0.00660
49b	10-S3-A4	5.52	124	2.39	0.182
19a	10-S3-F3	7.20	200	2.56	0.576
47	5-SIA-E4E	5.22	225	2.29	1.26
20	10-S3-F4	7.14	250	2.50	2.62
48	5-SIA-E4D	4.57	275	2.62	2.47

APPENDIX D

NON-LINEAR OXIDATION

A parabolic model by Pearce and Kay (1987) predicts the oxidation of clean uranium surfaces in dry air. The model was developed using test data in the temperature range 105 °C to 325 °C and takes the form

$$W = k_p \times t^{1/2} + k_l \times t \quad (D1)$$

where:

W is weight gain, t is time, and k_p and k_l are the parabolic and linear rate constants, respectively.

The rate constant values are calculated using the following rate law equations:

$$\log k_p = 3.679 - 1922/T \quad (D2)$$

and

$$\log k_l = 8.946 - 4638/T \quad (D3)$$

with k_p expressed in units of mg weight gain cm^2/hr and k_l in units of $\text{mg}/\text{cm}^2/\text{hr}$. T is the temperature in degrees Kelvin. A similar parabolic model has been reported by Colmenaries (1984) using different rate law equations.

Weight gain curves for oxidation of uranium in dry air at 90 °C and 200 °C using Equations (D1) (D2) and (D3) are shown on Figure D1. The time of exposure (8 hours) is similar to that expected for Cold Vacuum Drying (CVD) of an MCO containing typical K Basin SNF. Average linear oxidation between 3 and 8 hours is shown on the plots. The slope of this pseudo-linear oxidation is compared to the linear constant (k_l) for the oxidation plot (see Figure D1). Note that the ratio of the pseudo-linear oxidation rate to k_l is substantially higher at 70 °C than at 200 °C. If only the linear rate represented by the linear oxidation from 3 to 8 hours were used in a calculation of oxidation for the clean uranium represented in these plots, substantial oxidation would not be calculated for the first 2 hours of exposure.

K Basin SNF samples have been tested in dry air and the results were reported by Abrefah, et al. (1998) and are listed in Appendix C of this document. The surfaces of the samples used in the tests were as cut, that is they were not cleaned of oxide that may have existed from the cutting operations or exposure to ambient air after cutting. Thus, a thin, unknown thickness of oxide covered the test surfaces at the initiation of the oxidation tests. This oxide coating was certainly much less than that of a long exposed surface of a failed fuel element stored in the K Basin water for the typical 10 to 20 years. It may not, however, be very different than

freshly exposed surfaces resulting from preparations of the fuel for loading into an MCO. If it becomes necessary for the Spent Nuclear Fuel Project to consider oxidation of relatively unoxidized surfaces, a method for accomplishing this will be needed. One possible strategy is outlined in the following discussion.

Figure D2 shows the data from SNF test runs at 90 °C and 124 °C. These oxidation curves show non-linear oxidation in the first few hours of the test. The linear oxidation rates from Appendix C are shown on the plots as bold lines fit to the later portion of the curves. A line extends from the origin and intersects the bold line at 2 hours. This represents the mean linear oxidation rate between time zero and 2 hours exposure. Each of the SNF data curves were evaluated in this way with the initial-linear rate constants (k_i) and the final-linear rate constants (k_f) plotted on Figure D3. Linear regression analyses of $\log(\text{rate})$ versus inverse temperature ($1/T$) were performed to derive equations for the rate constants. Equations for the upper and lower bounds were determined using the mean of the 95% prediction intervals. These equations are applicable only at temperature below 287 °C (560 K). Above 560 K, $k_i \cong k_f$, and the one step linear oxidation equations given in the main body of this document may be used for clean surface without significant penalty.

For Process Calculations

$$\log k_i = 2.235 - 935.5/T \text{ for } t \leq 2 \text{ hr and } T \leq 560 \text{ K}$$

$$\log k_f = 4.451 - 2177/T \text{ for } t \geq 2 \text{ hr}$$

$$k_i = k_f \text{ at } T > 560 \text{ K}$$

Upper Bound for Safety Basis

$$\log k_i = 2.985 - 935.5/T \text{ for } t \leq 2 \text{ hr and } T \leq 494 \text{ K}$$

$$k_i = k_f \text{ at } T > 494 \text{ K}$$

$$\log k_f = 5.499 - 2177/T \text{ for } t \geq 2 \text{ hr}$$

Lower Bound for Safety Basis

$$\log k_i = 1.485 - 935.5/T \text{ for } t \leq 2 \text{ hr and } T \leq 560 \text{ K}$$

$$\log k_f = 3.402 - 2177/T \text{ for } t \geq 2 \text{ hr}$$

where:

k is rate of weight gain in $\text{mg}/\text{cm}^2/\text{hr}$, t is time in hours and T is temperature in degrees Kelvin.

References

- 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.
- Colmenares, C. A., 1984, "Oxidation of Mechanisms and Catalytic Properties of the Actinides," *Progress in Solid State Chemistry*, Vol. 15, pp. 257-364.
- Pearce, R. J., and P. Kay, 1987, *The Reaction of Uranium in the U-O₂-H₂O and U-H₂O Systems*, TPRD/B/0954/R87, Central Electric Generating Board, Berkeley Nuclear Laboratories, United Kingdom.

Figure D1. Oxidation of Uranium in Dry Air at 70 °C and 200 °C as Predicted by Pearce and Kay (1987).

Figure D2. Evaluation of Oxidation Data from K Basin Fuel Tests at 90 °C and 124 °C for Two-Step Linear Oxidation Rate Data.

Figure D3. Arrhenius Plot of Two-Step Linear Oxidation Rate Data from K Basin Fuel Tests.

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