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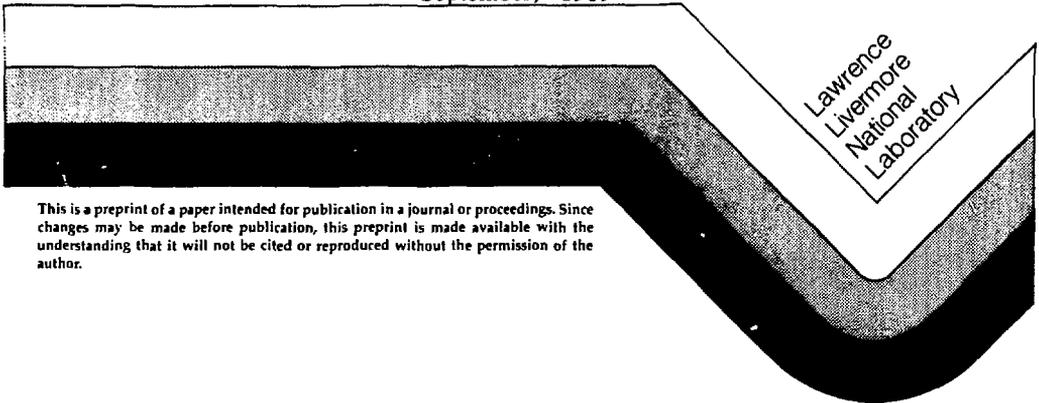
**STATISTICAL MODEL FOR GRAIN BOUNDARY AND
GRAIN VOLUME OXIDATION KINETICS IN UO_2 SPENT FUEL**

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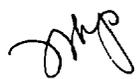
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ABSTRACT

The Yucca Mountain Project of the U.S. Department of Energy is investigating the suitability of a site in the unsaturated zone at Yucca Mountain, NV, for a high-level nuclear waste repository. Most of the waste will consist of UO_2 spent fuel in Zircaloy-clad rods from nuclear reactors. If failure of both the waste containers and the cladding occurs within the lifetime of the repository, then the UO_2 will be exposed to oxygen in the air and higher oxides of uranium may form. The oxidation state of the spent fuel may affect its dissolution behavior if later contacted by water. A model for the kinetics of spent fuel oxidation under repository-relevant conditions is thus necessary to predict the behavior of the waste form for assessing the performance of the repository with respect to the containment of radionuclides. In spent fuel experiments, the UO_2 oxidation front initially propagates along grain boundaries followed by propagation into grain volumes. Thus, the oxidation kinetics is controlled by two processes and the oxidation of spent fuel fragments will depend on the density and physical attributes of grain boundaries. With this in mind, concepts from statistical mechanics are used to define a density function for grain boundaries per unit volume per unit species in a spent fuel fragment. *Combining the integral forms of mass conservation and this grain boundary density function, a model for the global rate of oxidation for a spent fuel fragment is obtained. For rapid grain boundary oxidation compared to grain volume oxidation, equations of the model are solved and results compared to existing data.*

INTRODUCTION

In any proposed nuclear waste repository for spent fuel from nuclear power reactors, the potential release rates of many radionuclides over a 10000 year design lifetime depends on the oxidation rate and the oxidation state of any irradiated UO_2 fuel pellets that may be exposed to the atmosphere [Einziger and Woodley, 1985; Einziger, 1985; Oversby, 1987]. This is because the oxidization state of UO_2 , into U_3O_7 or possibly other oxides, could influence the low temperature dissolution rates of any spent fuel that may be exposed to water in a repository. Therefore, experiments to provide both data and a physical basis for rational model development for UO_2 oxidation kinetics are necessary in order to eventually predict potential radionuclide release rates from spent fuel in a repository.

Experimental tests of spent fuel oxidation to provide data and to identify a physical basis for model development were proposed by Einziger [1986a, 1986b]. Results from the tests completed [Einziger, et al., 1987; 1988] at this time imply that the grain boundaries of irradiated UO_2 oxidized more rapidly than the grain volumes at low temperatures (100 to 200°C). These grain boundary and grain volume observations agreed with other experimental observations made at similar and slightly higher temperatures [Aronson, et al., 1957; Wood, et al. 1987]. This two-rate oxidation process of UO_2 spent fuel is difficult to represent mathematically because classical diffusion models with their associated classical initial conditions and external boundary conditions do not physically describe certain geometrical aspects of the experimental observations.

To illustrate the difficulties, consider the observations on a fragment from a typically fractured UO_2 pellet taken from a spent fuel rod. Ceramographic and transmission electron microscopic examinations show one oxidation "front" that propagates from the external surface into the fragment along grain boundaries [Thomas, et al. 1989, Wood, et al. 1987]. As this grain boundary oxidation front proceeds inwardly, the grain boundaries are observed to crack apart; thereby creating opened flow

pathways for oxygen transport to all surfaces of all grain volumes behind the grain boundary oxidation front. The cracks propagate along the planes defined by sets of grain boundaries because, at low temperatures, the UO_2 of the grain boundaries is oxidized first to U_3O_7 , which has an incremental increase in density of about 3%. This incremental density increase means that the grain boundaries have a "tensile" strain field induced in their thickness direction because the individual grain volumes, on the average, are stationary as the grain boundary oxidation front propagates past. This "tensile" strain field, particularly in the thickness direction of a grain boundary, results in a sufficiently large tensile stress state to propagate cracks along the grain boundaries.

While the grain boundary oxidation front and grain boundary cracks propagate into a fragment of a spent fuel pellet, the set of grain volumes behind the front are commencing to oxidize. Because the external surface of these grain volumes are now exposed, they are observed to oxidize to U_3O_7 by a second type of oxidation front propagating into the volume of each grain. This grain volume oxidation front appears to remain approximately self-similar to the outer geometrical shape of the grain volume, and is, therefore, defined by the geometrical shape of the grain boundaries surrounding a grain volume. Thus, the physical characteristics and number density of grain boundaries and their associated grain volumes are important primitive function variables in mathematically representing low temperature oxidation kinetics of UO_2 spent fuel.

Classical diffusion models [Carslaw and Jaeger, 1959; Gleiter and Chalmers, 1972] do not explicitly incorporate a dependence on diffusional differences and the geometrical attributes of grain boundaries and grain volumes. There exists a dual diffusion model by Olander [1986] that has been used to empirically represent some experimental data [Einziger, et al. 1987]. However, the dual diffusion model is not readily adapted to represent a statistical number density of different grain boundaries and grain volumes spatially distributed in a fragment of given size and shape from a spent fuel pellet. Furthermore, the next complexity in oxidation kinetics modelling is a statistical representation for the number density for the sizes and shapes of different fragments that can be typically expected

in an oxidation testing experiment and from fractured fuel pellets exposed after container and fuel rod cladding failures occur in a repository environment. The latter density function for fragment distribution enters into some low temperature experimental planning [Einziger, 1986a, 1986b], because it has been observed that the time response of UO_2 oxidation along grain boundaries and into grain volumes are interdependent for large fragments and small grain sizes.

This interdependence exists because the grain boundary oxidation front is observed to propagate more rapidly into a fragment than the grain volume oxidation front propagates into a grain at a given temperature. Thus, for small fragments, the grain boundary oxidation process is completed in a short time interval, and this time interval can be neglected in comparison to the time interval of the subsequent grain volume oxidation. However, for larger fragments, the time interval for grain boundary oxidation may be sufficiently long that significant grain volume oxidation has occurred in a spatial neighborhood near the exterior surface of a fragment. In fact, for small grain sizes relative to the fragment size, the complete oxidation of grain volumes near the outer perimeter of a fragment may have occurred before the grain boundary oxidation front has propagated completely across the fragment. Thus, a reasonably complete model for oxidation kinetics should be able to represent the above situations for small and large fragments relative to small and large grain sizes. In this short article, only the case of a small sized fragment and large grain sizes will be analyzed in detail. This is completed in the next section. The approach is to statistically describe grain boundary segments and their associated grain volumes. This statistical approach is refined in a later section to provide a brief qualitative description for oxidation kinetics of large sized fragments and small grains. Also, there is a brief discussion for a statistics of fragments from spent fuel pellets.

In brief, this short paper addresses statistical characteristics for the simplest case of grain boundary/grain volume oxidation kinetics of UO_2 to U_3O_7 for a fragment of a spent fuel pellet. It also presents a limited discussion of future extensions to this simple case to represent the more complex cases of oxidation kinetics in spent fuels.

STATISTICAL DESCRIPTION OF GRAIN BOUNDARY/VOLUME OXIDATION PROCESSES

In describing a statistical approach to model grain boundary/volume oxidation processes, the first step is assigning a set of physical attributes to identify the various species of grain boundaries and grain volumes that arise during oxidation. At the least, the physical attributes should be descriptive of the planes of grain boundaries and associated pyramidal grain volume segments that are being oxidized in a given fragment. To assign physical attributes for grains in a fragment of a UO_2 pellet, the boundaries of an arbitrary grain are assumed to consist of a set of planar area segments. The size and orientation for each area segment can be effectively described by two orthogonal vectors \underline{a} and \underline{b} . Also, the vectors \underline{a} and \underline{b} can be chosen such that their cross product is directed into the grain; and this vector would be normal to the area segment of the grain boundary. For a given segment with vectors \underline{a} and \underline{b} , a vector \underline{c} can be chosen that measures the perpendicular distance from the area segment to the center of the grain volume. By assigning vectors \underline{a} , \underline{b} , and \underline{c} around the boundary of every grain in a fragment, the total spatial volume of a fragment can be decomposed into a set of pyramidal volumes, some of which may be oxidized, some may be partially oxidized and are presently oxidizing, and some may remain to be oxidized. To characterize the later three species, additional physical attributes are chosen. The degree of oxidation of a grain boundary/volume species can be described with three scalar variables, A, B, and C, which have values on domain (-1.0, 1.0) to measure the fractional lengths of the vectors \underline{a} , \underline{b} , and \underline{c} that have been oxidized. Finally, the rate of oxidation can be described by three rate variables, \dot{A} , \dot{B} , and \dot{C} , where \dot{A} and \dot{B} describe the rate at which a grain boundary is being oxidized along vectors \underline{a} and \underline{b} , respectively, and \dot{C} describes the rate that a grain volume is being oxidized along vector \underline{c} . The units chosen for \dot{A} , \dot{B} , and \dot{C} are per unit time only, and the velocities of oxidation are expressed in units of their corresponding vectors. Thus, along vectors \underline{a} , \underline{b} , and \underline{c} , the oxidation process propagates at velocities $\dot{A}\underline{a}$, $\dot{B}\underline{b}$, and $\dot{C}\underline{c}$, respectively. The net result of using this definition to express oxidation velocities along grain boundaries and into grain volumes, is a construction of local, intrinsic sets of basis vectors (\underline{a} , \underline{b} , \underline{c}) for each

pyramidal volume in all grains contained in a fragment from a spent fuel pellet. Given a set of basis vectors, $(\underline{a}, \underline{b}, \underline{c})$ and their associated scalar variables $(A, B, C, \dot{A}, \dot{B}, \dot{C})$, one can identify and count various grain boundary/volume species in a unit spatial volume of a fragment. This process can be used to construct a probability density function for the various grain boundary/volume species according to their current values of $(\underline{a}, \underline{b}, \underline{c}, A, B, C, \dot{A}, \dot{B}, \dot{C})$ at some arbitrary time t . For example, if oxidation has not yet begun in a spatial volume neighborhood about point \underline{x} at time t , then the various species would be identified as a subset $(\underline{a}, \underline{b}, \underline{c}, 0, 0, 0, 0, 0, 0)$. Also, if oxidation of the grain boundaries and grain volumes were completed about point \underline{x} at time t , then the various species would be identified as a subset of $(\underline{a}, \underline{b}, \underline{c}, \pm 1, \pm 1, 1, 0, 0, 0)$. Any other state of UO_2 oxidation to U_3O_7 would have values other than 0 or ± 1 . for some values of $(A, B, C, \dot{A}, \dot{B}, \dot{C})$ which would indicate the oxidation process is in progress.

To make analytical use of this approach that identifies grain boundary/volume species, a probability density function $G(\underline{x}, t, \underline{a}, \underline{b}, \underline{c}, A, B, C, \dot{A}, \dot{B}, \dot{C})$ is defined, which gives the number of grain boundary/volume species with values $(\underline{a}, \underline{b}, \underline{c}, A, B, C, \dot{A}, \dot{B}, \dot{C})$ per unit spatial volume per unit species volume at point \underline{x} and time t . For shorthand purposes, the set of species variables $(\underline{a}, \underline{b}, \underline{c}, A, B, C, \dot{A}, \dot{B}, \dot{C})$ will be denoted by a matrix variable g ; then the species density function becomes $G(\underline{x}, t, g)$.

From the above discussion, the species density function evolves in time as the grain boundary oxidation front propagates past a spatial point \underline{x} . It is natural to seek a field equation that describes, in a general sense, the evolution of the species density function. Such an equation exists, and it is an analog to the classical Boltzmann equation from the kinetic theory of gases [Boltzmann, 1964] as well as an analog to field equations describing dislocation density kinetics, microcrack/density kinetics, and particle-void kinetics [Stout, 1981; Stout and Thigpen, 1984; Stout, 1989]. This evolution equation is a balance statement for the time rate of change of G at a given spatial point \underline{x} , and given species g ; it is

$$\partial_t G(\underline{x}, t, \underline{g}) + \nabla \cdot (\underline{v}G) = K^+(\underline{x}, t, \underline{g}^* \rightarrow \underline{g}) - K^-(\underline{x}, t, \underline{g} \rightarrow \underline{g}^*) \quad (1)$$

where \underline{v} is the velocity of material at point \underline{x} and time t , K^+ denotes a functional to represent the rate of transitions of grain boundary/volume species \underline{g}^* going into species \underline{g} , and K^- denotes a functional to represent the rate of transitions from species \underline{g} out to all other species \underline{g}^* . As will be seen, no explicit solution nor representations for K^+ and K^- are required for the analysis completed in this paper. This is because the physical assumptions made for the form of the species density function G make the evolution part of the oxidation kinetics problem into one of statistical bookkeeping.

For the first and simplest part of the oxidation problem, consider the case where \hat{A} and \hat{B} are large compared to \hat{C} (for regular shaped grains the magnitudes of vectors \underline{a} , \underline{b} , and \underline{c} are taken as nearly equal). Then, for small fragments the grain boundary oxidation front process is completed in a negligibly short time interval relative to the time interval for the grain volume oxidation front to propagate along the vector \underline{c} to the center of a typical grain. This leaves oxidation of grain volumes to analyze.

For a given fragment with volume V_f , let the function $N(\underline{x}, t)$ denote the number density of oxygen atoms per unit spatial volume at point \underline{x} in V_f and time t above the initial number density of oxygen atoms in the UO_2 spent fuel. Then the time rate of change of oxygen atoms in the fragment of a fixed spatial volume V_f is

$$\partial_t \int_{V_f} N(\underline{x}, t) dV = \int_{V_f} \partial_t N(\underline{x}, t) dV \quad (2)$$

because the fragment volume is approximately independent of time for the reasonably small deformations that occur when UO_2 is oxidized to U_3O_7 . By a previous assumption, the grain boundary oxidation is completed, and therefore, the rate of oxygen accumulation in V_f is by grain volume oxidation only. Let N_B be the value of N along all grain boundaries in V_f , and let N_F be the value of N along all grain volume oxidation fronts

propagating into the grains. Then, the time rate of change of N in V_f for all grain boundary/volume species in domain $\{g\}$ is approximately

$$\partial_t \int_{V_f} N dV = \int_{V_f} \int_{\{g\}} (N_F c_{ijk} a_j b_k (1-C)(1-C)\dot{C} + (N_B - N_F) c_{ijk} a_j b_k (6-8C + 3C^2)/12)\dot{C}) G(x,t,g) dg dV \quad (3)$$

where the first term on the right of the equal sign is the oxygen storage rate for a species at the grain volume oxidation front of area $e_{ijk} a_j b_k (1-C)(1-C)$ propagating into the grain volume at a rate \dot{C} ; (e_{ijk} is the Cartesian alternating tensor used to form the cross product of vectors \underline{a} and \underline{b}) and the second term is approximately the oxygen storage rate from a linear gradient approximation $(N_B - N_F)$ across the currently oxidized thickness of the grain which is changing in volume at a rate of $c_{ijk} a_j b_k ((6-8C+3C^2)/12)\dot{C}$. The first term described above accounts for the rate of oxygen atoms used to convert UO_2 to U_3O_7 at the oxidation front. The second term accounts for the rate of oxygen atoms used to maintain a linear gradient of oxygen atoms in the U_3O_7 between the grain boundary and the grain volume oxidation front.

For the case being considered, the grain boundaries are all oxidized during a short time interval, say $(0, t_{gf})$, and the grain boundary density function evolves to be $G(x, t_g, \underline{a}, \underline{b}, \underline{c}, \pm 1, \pm 1, 0, 0, 0, C)$ at time $t = t_{gf}$ for all points \underline{x} in fragment volume V_f . Then, neglecting the oxygen stored during the grain boundary oxidation time interval, a time integration of equation (3) gives formally

$$\int_{V_f} N(\underline{x}, t) dV = \int_{t_g}^t \int_{V_f} \int_{\{g\}} (N_F(1-C)(1-C) + (N_B - N_F)(6-8C+3C^2)/12) \dot{C} c_{ijk} a_j b_k G(\underline{x}, \tau, g) dg dV d\tau \quad (4)$$

In small fragments, it is reasonable to assume that the variance is small and spatially uniform for the different grain boundary/volume species in V_f . Furthermore, it is assumed that the grain boundary/volume density function is separable in a vector sense and is also spatially uniform in the physical attributes of $\underline{a}, \underline{b}, \underline{c}, C$, and \dot{C} in V_f . Then a Dirac delta function

at the mean value of each variable, namely $(\bar{a}, \bar{b}, \bar{c}, \bar{C})$, becomes a reasonable simplification to permit the integration over the species $\{g\}$ in equation (4) to obtain

$$N_f(t) = \int_{\omega} (N_F(1-\bar{C})(1-\bar{C}) + (N_B - N_F)(6 - 8\bar{C} + 3\bar{C}^2)/12) \bar{C} \bar{c}_{ijk} \bar{a} \bar{b} \bar{G}(\tau) d\tau \quad (5)$$

where $N_f(t)$ denotes the oxygen stored in the fragment with V_f volume at time t , and $\bar{G}(\tau)$ is the total number of grain boundary/volume species at time τ with physical attribute averages of $(\bar{a}, \bar{b}, \bar{c}, \bar{C})$. The time dependence from $\bar{G}(\tau)$ can be switched to the \bar{C} variable; then $\bar{C}\bar{G}(\tau)$ can be written as $\bar{C}(\tau)\bar{G}_f$ where G_f is the total number of all grain boundary/volume species in the fragment with V_f volume. Then equation (5) can be integrated with respect to time to obtain

$$\begin{aligned} N_f(t) = & N_F \bar{c}_{ijk} \bar{a} \bar{b} G_f (3\bar{C}(t) - 3\bar{C}^2(t) + \bar{C}^3(t))/3 \\ & + (N_B - N_F) \bar{c}_{ijk} \bar{a} \bar{b} G_f (6\bar{C}(t) - 4\bar{C}^2(t) + \bar{C}^3(t))/12 \end{aligned} \quad (6)$$

where
$$C(t) = \int_{\omega} \bar{C}(\tau) d\tau \quad (7)$$

and the initial condition for C at time $\tau = t_{gf}$ is

$$\bar{C}(t_{gf}) = 0 \quad (8)$$

In equation (6) it is noted that the fragment volume V_f is also the average pyramidal volume multiplied by the number of pyramids in the fragment;

$$V_f = \bar{c}_{ijk} \bar{a} \bar{b} G_f / 3 \quad (9)$$

Then by dividing equation (6) by $N_F V_f$ and adding unity to each side, equation (6) can be written as

$$(1 - N_f(t)/N_F V_f) = (1 - 3\bar{C} + 3\bar{C}^2 - \bar{C}^3) + (N_B - N_F)(6\bar{C} - 4\bar{C}^2 + \bar{C}^3)/(4N_F) \quad (10a)$$

$$= (1 - \bar{C})^3 + (N_B - N_F)\bar{C}(6 - 4\bar{C} + \bar{C}^2)/(4N_F) \quad (10b)$$

When the ratio $(N_B - N_F)/N_F$ is small and/or at early times when the grain volume oxidation front has propagated only a small fraction of the length of vector \bar{e} (i.e., $\bar{C}(t)$ is small), then the second term in equation (10b) containing \bar{C} can be neglected compared to the first term, and the following approximation is obtained:

$$(1 - N_f(t)/N_F V_f) \doteq (1 - \bar{C})^3 \quad (11)$$

Equation (11) can be rewritten in the following form,

$$1 - (1 - N_f(t)/N_F V_f)^{1/3} = \bar{C}(t) \quad (12)$$

which is essentially the same form used by Einziger and Woodley [1985] to correlate with experimental data as illustrated in Figure 1, providing

$$\bar{C}(t) = (kt)^{1/3} \quad (13a)$$

$$N_f(t)/N_F V_f = 3\Delta(O/M) \quad (13b)$$

where k is an empirical rate constant for grain volume oxidation of UO_2 to U_3O_7 that has been determined by data correlations [Einziger and Woodley, 1985], and $3\Delta(O/M)$ is a fractional measure for conversion of UO_2 to U_3O_7 that is based on the initial number of UO_2 molecules in volume V_f . To show the equivalence for equation (13b), recall that $N_f(t)$ is the number of oxygen atoms stored in fragment volume V_f and that N_F is the number of oxygen atoms per unit volume above the reference level of oxygen atoms in UO_2 . Furthermore, to stoichiometrically convert UO_2 to U_3O_7 , one oxygen atom must be added for every three molecules of UO_2 . Then, the value of N_F should be equal to one-third of the atomic number density of UO_2 molecules, N_{UO_2} , and equation (13b) can be written as

$$N_f(t)/(N_F V_f) = N_f(t)/(N_{UO_2} V_f/3) = 3N_f(t)/N_{UO_2} V_f \quad (14)$$

which represents the number of oxygen atoms in volume V_f converted to U_3O_7 molecules, divided by the initial number of UO_2 molecules in volume V_f ; hence

$$N_f(t)/(N_f V_f) = 3\Delta(O/M) \quad (15)$$

Substituting from equations (14) and (15) into equation (13), the following expression is obtained

$$1 - (1 - 3\Delta(O/M))^{1/3} = (kt)^{1/2} \quad (16)$$

Equation (16) has been shown to correlate with experimental data for small fragments and large grain sizes [Einziger and Woodley, 1985]. For these geometrical conditions, the experimental data provide support for the approximations used in representing statistically the slower oxidation of grain volumes relative to the more rapid oxidation of grain boundaries. In the above analysis to derive equation (12), it is noted that only the rate of change of oxygen for the volume integral was used. It is known that the complete balance equation for a mass transport has the following form [Slattery, 1972],

$$\partial_t \int_{V_f} N(\underline{x}, t) dV = - \int_{A_{f0}} \underline{v}_N N \cdot \underline{n}_0 dA \quad (17)$$

where $\underline{v}_N N$ is the flux of oxygen atoms crossing the initial exterior boundary A_{f0} of spatial volume V_f , and \underline{n}_0 is the outwardly directed unit normal vector on boundary A_{f0} for a stationary, non-deforming fragment.

At first, equation (17) does not appear too useful because a representation for the flux of oxygen on A_{f0} as the grain boundaries intersecting A_{f0} , crack apart is not analytically tractable. However, another viewpoint for the area dependence of equation (17) is to consider the instantaneous area that is exposed to oxygen flux into grain volumes as the grain boundary oxidation front propagates through the fragment volume V_f . Then, equation (17) can be written as

$$\partial_t \int_{V_f} N(\underline{x}, t) dV = - \int_{A_f(t)} \underline{v}_N N \cdot \underline{n} dA \quad (18)$$

where now $\underline{v}_N N$ is the oxygen flux crossing all exposed area $A_f(t)$ at time t in the fragment volume V_f , and \underline{n} is the outwardly directed unit normal vector on $A_f(t)$. A general expression for area $A_f(t)$ can be written, however, in order to write such an expression for $A_f(t)$ as a function of time during the time interval for the grain boundary oxidation front to propagate throughout the volume domain V_f , detailed information about the fragment geometry is required. This topic will be discussed later. For now, one of the assumptions under which equation (12) was developed from equation (4) was that the time interval $(0, t_{gf})$ for completion of grain boundary oxidation was neglectably small in comparison to the subsequent time interval for grain volume oxidation. Thus, consistent with equation (12), equation (18) can be written as

$$\partial_t \int_{V_f} N(\underline{x}, t) = - \int_{A_f(t_{gf})} \underline{v}_N N \cdot \underline{n} dA \quad (19)$$

where the area $A_f(t_{gf})$ is the total exterior area of all grain volumes which is a constant for times t greater than t_{gf} . Using this area, then a relationship for the flux on $A_f(t_{gf})$ can be written for diffusional transport as

$$\underline{v}_N N(\underline{x}, t) = - D \nabla N(\underline{x}, t) \quad (20)$$

for \underline{x} on $A_f(t_{gf})$ and where D is the diffusion coefficient for oxygen transport through U_3O_7 . Equation (20) requires an expression for the gradient of the oxygen concentration along the grain surfaces $A_f(t_{gf})$; which is not readily approximated because the gradients normal to the boundaries in neighborhoods of the exterior corners and edges are approximately zero when the oxygen concentration is uniformly equal to N_B on the boundary surface. This leaves one last form to write equation (19), which is in the form for oxygen flux crossing the grain volume oxidation front at time t for all grains in volume V_f . This means that the area will again be time dependent, however, a simple approximation can be made to express the gradient operator in equation (20) at the grain

volume oxidation front in each grain. To develop the expression for oxygen flux at the grain volume oxidation front, consider a generic pyramidal volume of a grain; the oxidation front is presumed to have progressed to a value C along vector \underline{c} ; then the vector area of the oxidation for this front is

$$\Delta A_i = \epsilon_{ij} a_j (1 - C) b_k (1 - C) \quad (21)$$

where the exterior area is decreased by the factor $(1 - C)$ on each exterior vector dimension by reason of linear geometrical similarity.

The gradient operator across the thickness of U_3O_7 between the exterior area at $C = 0$ and the value C normal to both the exterior area and the volume oxidation front area is approximated by

$$\nabla N \cdot \frac{\underline{c}}{|\underline{c}|} = \partial_i N \frac{c_i}{|\underline{c}|} = \frac{N_B - N_F}{C |\underline{c}|} \frac{c_i}{|\underline{c}|} = \frac{(N_B - N_F)}{C c_m c_m} c_i \quad (22)$$

where $|\underline{c}|$ denotes the magnitude of vector \underline{c} and $(N_B - N_F)$ is the difference between the values of oxygen concentration on the exterior grain boundary and the grain volume oxidation front. This difference divided by the distance between the boundary and the front; $\frac{C}{|\underline{c}|}$ is a reasonable approximation to the oxygen concentration gradient normal to the grain volume oxidation front. With equations (20), (21), and (22), equation (18) can be expressed in terms of a double integral for all species of grain volume oxidation fronts by multiplying by their number density per unit volume per unit species and integrating over the species domain $\{g\}$ in a fragment volume V_f , which is

$$\partial_t \int_{V_f} \int_{\{g\}} D \frac{(N_B - N_F)}{C c_m c_m} \epsilon_{ij} a_j b_k (1 - C)^2 G(\underline{x}, t, g) dg dV \quad (23)$$

for times t greater than time t_{fg} .

The next step is to equate the first term on the right hand side of equation (3) to equation (23) (since the second term in equation (3) was

assumed neglectable in the subsequent analysis to arrive at equation (17) that compared well with experimental data); for $t > t_{gf}$, this gives

$$\partial_t \int_{v_r} \int_{t_{el}} N_F c_{ij} a_j b_k (1-C)^2 \dot{C} G(x,t,g) dg dV \quad (24a)$$

$$= \int_{v_r} \int_{t_{el}} \frac{D(N_B - N_F)}{C c_m c_m} c_{ij} a_j b_k (1-C)^2 G(x,t,g) dg dV \quad (24b)$$

Equations (24a) and (24b) can be rearranged and written as

$$0 = \int_{v_r} \int_{t_{el}} (N_F \dot{C} - \frac{D(N_B - N_F)}{C c_m c_m}) c_{ij} a_j b_k (1-C)^2 G(x,t,g) dg dV \quad (25)$$

Within the context of the approximations leading up to it, equation (25) is true for all grain boundary/volume density functions G ; therefore, equation (25) implies that for every grain boundary/volume species

$$N_F \dot{C} - \frac{D(N_B - N_F)}{C c_m c_m} = 0 \quad (26)$$

Subject to the given assumptions that N_F , N_B , D , and c are independent of time, then the only time dependence possible for the evolution of C is the square root function; thus, for any species, equation (26) is true if

$$C(t) \propto \sqrt{t} \quad (27)$$

In view of equation (13a), the proportionality coefficient for a generic species ($C c_m$) in equation (27) is taken as the square root of k_c , which can be used to convert expression (27) into an equality that can be substituted into equation (26) to find a value of k_c given by

$$k_c = D(N_B - N_F)/(N_F c_m c_m) \quad (28)$$

where D is the diffusion coefficient of oxygen through U_3O_7 , N_B is the value of oxygen concentration at the grain boundary, N_F is the value of oxygen concentration at the grain volume oxidation front (both N_B and N_F are

referenced at zero oxygen concentration in pure UO_2), and c_m is a physical attribute for the pyramidal height of a grain boundary/volume species. Experimentally, it would be expected that the empirical value measured for k would be representative of all species, and an analytical estimate of k for equation (13a) could be approximated with equation (28) as

$$k \approx D(N_B - N_F)/(N_F \bar{c}_m \bar{c}_m) \quad (29)$$

The above analysis has provided a physical interpretation for the empirical parameter k for oxidation rate kinetics of UO_2 to U_3O_7 . The analysis is only a first and perhaps easiest step in model development of oxidation kinetics of UO_2 spent fuel. Future directions in model development are briefly discussed in the next section.

UO₂ SPENT FUEL OXIDATION MODEL DEVELOPMENT IN PROGRESS

The above statistical analysis treated a particular case for the oxidation kinetics of small fragments and large grain sized UO_2 oxidized to U_3O_7 . There remains several cases to analyze, namely:

- Case 1. oxidation kinetics that occur during the initial grain boundary oxidation front time interval,
- Case 2. oxidation kinetics that occur in large fragments and small grain sizes,
- Case 3. oxidation kinetics that occur in a mixture of large and small fragment sizes,
- Case 4. oxidation kinetics for other oxidation states of UO_2 spent fuel.

Case 1

The analysis of case 1 is tractable as a one dimensional, initial value problem in an early part of the time interval $(0, t_{gf})$ during which the oxygen concentration on the grain surface of a grain volume evolves from $N = 0$ to $N = N_B$. The analysis will require a couple of assumptions, one of which is an estimate for the flux of oxygen at the surface of the grain

volume. Note that an estimate for the value of N_B can be made from equation (28); and an estimate for the time interval can be obtained from experimental data. Since solutions for this class of initial value problem are available, the total oxygen ingress during an early part of the time interval $(0, t_{gf})$ can be calculated for a small fragment. Thus, available experiment data of total weight gain for a known number of small fragments and grain sizes can be used to obtain an estimate of oxygen flux at the surface of grains during the early part of the time interval in which grain boundary oxidation occurs.

Case 2

In case 2, the time interval during which the grain boundary oxidation is completed is sufficiently long for a large fragment that some of the perimeter grain volumes around the exterior surface of a fragment are near, or completely, oxidized to U_3O_7 . To analyze this case, one must first model the time dependence of the grain boundary oxidation front propagating across a fragment. This is presently believed to be feasible by representing the probable propagation velocity of the grain boundary oxidation front, v_{gbof} , along normals n_f to the exterior boundary of a fragment as

$$n_f \cdot v_{gbof} = n_f \cdot (\dot{A} \underline{a} + \dot{B} \underline{b}) G(\underline{x}, t, g) \quad (30)$$

where estimated values for \dot{A} and \dot{B} are required from experimental methods. Then, a unit step function can be used in the integrands of oxygen ingress expressions to demarcate a time dependent spatial domain of integration within a given fragment of given geometrical characteristics. Furthermore, for nearly uniform grain sizes and large fragments, a second oxidation front propagates from the exterior boundary across a fragment volume as the oxidation of grain volumes is completed. For nearly uniform grain sizes, this grain volume oxidation completion front is essentially a constant time-delay front that follows after the grain boundary oxidation front. Hence, its propagation velocity is the same as the grain boundary oxidation front and is time-delayed for the time interval it takes to

complete the grain volume oxidation. This latter time interval can be estimated from equation (14), which relates C and $(kt)^{1/2}$. Since grain volume oxidation is complete when C equals unity, the time-delay interval t_d is roughly

$$t_d \doteq 1/k \quad (31)$$

This time-delay interval provides estimates for limits of integrations over time during which oxygen ingress occurs into grain volumes at different spatial points in large fragments. Thus, the experimental data obtained from the simplified experiments of small fragments and large grains have provided immensely useful physical and mechanistic knowledge for further model development and future experimental designs.

Case 3

Case 3 is approaching a realistic oxidation situation that may occur in a repository, where a statistical distribution of all fragments of pellets in a fuel rod can be exposed to atmospheric air. In the previous discussions, model development has been described in terms of what happens to a given sized fragment. Now, the objective is a comprehensive model to treat a mixture of different sizes and shapes of fragments that are observed in a fuel rod. Conceptually, such a comprehensive model is analytically derived by first assigning physical attributes to identify the various sizes and shapes of fragments from a generic fuel rod; much like the assignment of physical attributes for grain boundaries and grain volumes.

For example, the shape of a typical fragment from a fractured spent fuel pellet can be approximated as a volume enclosed by a finite set of planar surface segments. In some cases, perhaps one segment of surface would be the cylindrical surface of a pellet and a class of wedge-shaped fragments identified. In any case, the perpendicular distance from a surface to the center of the fragment can be readily estimated. Thus, physical attributes which are vector dimensions for surfaces and the

perpendicular vector distances can be assigned for all fragments of all pellets in a typical fuel rod. Clearly, these vector dimensions are analogs to the physical attributes previously assigned to characterize pyramidal volume domains in a grain. Hence, a classification for different pyramidal volume species in a fragment has been defined, and then the number of pyramidal volume species per fragment can be identified and counted. This leads logically to a probabilistic definition for a "fragment" density function as the number of pyramidal volume species of a given size (surface vectors and perpendicular vector) per unit species per fuel rod. This fragment density function may also depend on some history parameters of the fuel rod, such as burn-up or fission gas release. These data for a fragment density function are only obtainable by careful characterization of spent fuels. With this type of data, the statistical analysis problem of treating mathematically an arbitrary fragment density function of a fuel rod can be readily completed by slightly modifying integral expressions for oxidation of a given fragment volume through decomposition of the fragment volume integration into a set of integrations over pyramidal volumes that progress one dimensionally from a planar exterior surface segment to the apex.

Case 4

Presently little progress has been made on detailed model development for the oxidation kinetics of spent fuel from U_3O_7 to higher states. One reason for this is that detailed and careful examination of low temperature spent fuel has not revealed the existence of an oxidation state greater than U_3O_7 . To attain a higher oxidation state, which requires a thermodynamic phase transformation, the oxygen concentration $N(\underline{x},t)$ must reach locally a sufficient high value, N^* , to convert U_3O_7 to the next phase. At low temperature, the attainment of concentration N^* is only possible if the chemical potential of oxygen in the atmosphere surrounding an exposed surface of U_3O_7 spent fuel is and remains greater than the chemical potential of oxygen in U_3O_7 spent fuel. Otherwise, oxygen will not enter into a U_3O_7 spent fuel fragment. This is but one possible conjecture

for not observing higher oxidation states of UO_2 other than U_3O_7 . Clearly, more carefully planned and controlled experiments are necessary to establish a basis of model development for the oxidation kinetics to higher oxidation states of spent fuel.

SUMMARY

Using small fragments from UO_2 spent fuel pellets, oxidation experiments have been performed that measured weight gain by thermogravimetric analysis techniques and spatial domains of different grain boundary and grain volume oxidation processes by ceramography. Based on these data and observations with other microscopic techniques, a statistical approach has been developed to represent grain boundary and grain volume oxidation processes for spent fuel from UO_2 to U_3O_7 . For small fragments, the statistical approach represents well the physically observed geometrical features of a grain boundary oxidation front propagating rapidly through a fragment followed by dense sets of grain volume oxidation fronts propagating more slowly across individual grains. Using the statistical formulation, equations are developed for this case that can be made equivalent to empirical expressions that have been used to correlate with existing experimental data. In showing this equivalence, phenomenological coefficients in the empirical expressions are given a physical interpretation in terms of the diffusion coefficient, grain size, and boundary values of oxygen concentration. As discussed in the future work section, this physical interpretation will be very useful in developing models that describe oxidation kinetics for the typical large fragments from UO_2 spent fuel pellets that can be expected in failed fuel rods.

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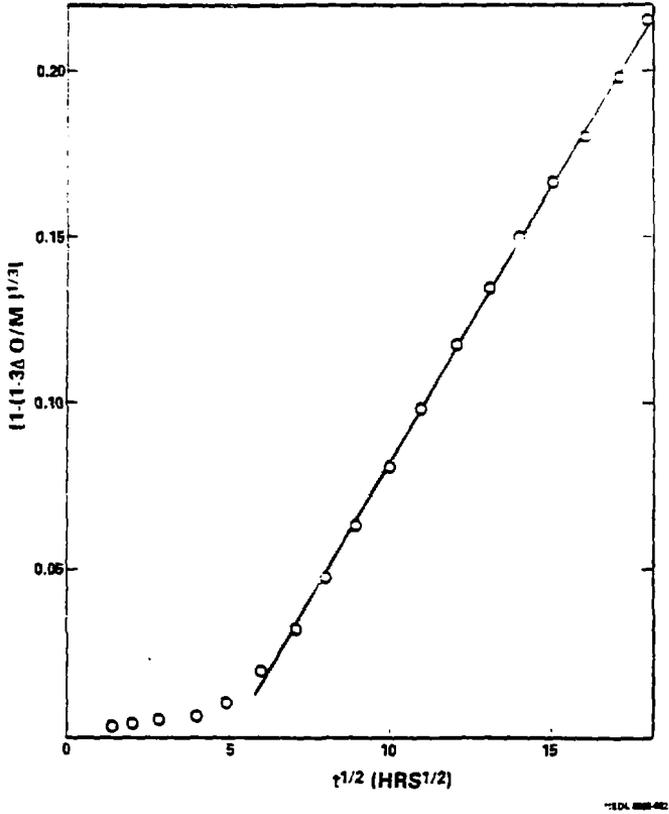


Figure 1. Oxidation of Spent Turkey Point PWR Fuel in Air at 200°C.
Measurement Error on the Data is Less than $\pm 5\%$ at Any Point.