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OSTI**KINEMATICS AND THERMODYNAMICS ACROSS A
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PHASE FRONT IN SPENT FUEL GRAINS**R.B. Stout
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KINEMATICS AND THERMODYNAMICS ACROSS A PROPAGATING NON-STOICHIOMETRIC OXIDATION PHASE FRONT IN SPENT FUEL GRAINS

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Spent fuel from power reactors contains mixtures, alloy subsets, and compounds of elements; but the aggregate atomic densities in spent fuel are dominated by uranium and oxygen atoms. With the exception of some UO_2 fuels with burnable poisons (primarily gadolinia in BWR rods), the other elements with significant atomic densities in spent fuel evolve during reactor operation from neutron reactions and fission plus fission decay events. Due to nuclear decay processes, the intrinsic chemical composition and activity of spent fuel will continue to evolve after it is removed from reactors as its radioactivity decays over time. During the time interval when the radioactivity levels are significant, which is the time interval relevant for design and for performance assessment of a geological repository, it is important to develop an understanding and to develop models that describe potential chemical responses in spent fuel and its potential degradational impacts on repository design and performance. One such potential impact is the oxidation response of spent fuel. The oxidation of spent fuel results in an initial phase change of the UO_2 lattice to a U_4O_9 lattice, and the next phase change is probably to U_3O_8 although it has not been observed yet at low temperatures ($<200^\circ\text{C}$). The U_4O_9 lattice is non-stoichiometric with a oxygen to uranium weight ratio (O/U) at ~ 2.4 . Preliminary indications are that the UO_2 has a O/U of ~ 2.4 at the time just before it transforms into the U_4O_9 phase.^[1,2] Also, in the oxygen weight gain versus time response, a plateau appears as the O/U approaches ~ 2.4 . Part of this plateau response is due to geometrical effects of a U_4O_9 phase change front propagating into UO_2 grain volumes. However, the plateau time response may be indicative of a metastable phase change delay kinetics or a diffusional related delay time until the oxygen density can attain a critical value to satisfy the stoichiometry and energy conditions for phase changes. In a previous paper and as a first step, a kinematic and thermodynamic analysis was developed to model spatially homogeneous oxidation phase transitions.^[3] However, the experimental data clearly show a front of U_4O_9 lattice structure propagating into grains of the UO_2 lattice structure. To describe this spatially inhomogeneous oxidation phase transition, as well as the expected U_3O_8 phase transition from the U_4O_9 lattice, lattice models are developed and spatially discontinuous kinematic and energetic expressions are derived. The approach will use concepts from statistical mechanics, discontinuum mechanics, and non-equilibrium thermodynamics. In addition, analytical techniques from shock wave analysis will be used to derive the surface discontinuity energetic expressions across the propagating oxidation phase front.

INTRODUCTION

Spent Fuel Oxidation

In this paper, oxidation phase transition results derived for homogeneous transformations^[3] of UO_2 to U_4O_9 and U_3O_8 are extended for the case of inhomogeneous transformations within grain volumes of UO_2 spent fuel. The inhomogeneous transformation of UO_2 to U_4O_9 is observed as a boundary front of U_4O_9 propagating into a grain of UO_2 . In the case of U_4O_9 transforming into U_3O_8 , it is believed that a boundary front of U_3O_8

will also propagate into a grain of U_4O_9 . For some temperature histories, it may be possible to have both types of phase fronts propagating simultaneously into a grain, or the U_4O_9 phase front be overtaken by the U_3O_8 phase front and disappear. These latter two cases will not be treated herein; only the isolated cases for a grain with a UO_2 and U_4O_9 phase front or for a grain with a U_4O_9 and U_3O_8 will be analyzed.

The notation and equations from the previous analysis of homogeneous phase transformation will be briefly reviewed in the following section. Essentially, the analysis is microscopic and

formulates the spent fuel oxidation problem as both kinematically and energetically dependent on lattice structure. The lattice structure contains associated lattice atoms and vacancies from fission events plus the addition of oxygen atoms responsible for the higher oxidation phase transitions from UO_2 spent fuel. Following this brief review, kinematic and energetic equations across propagating oxidation fronts will be developed. The energetic equation includes terms for the non-stoichiometric effects of oxygen in the lattice structure. In describing the evolution of the microscopic lattice structure through the phase changes, the mathematical description does not use the crystallographic lattice structure, but will use an idealized pseudo-lattice structure that has four uranium atoms per cell. Thus, a UO_2 cell is identified as U_4O_8 , and a cell of U_4O_9 forms from a U_4O_8 cell by the reaction of one additional oxygen atom. Finally, the U_3O_8 would be $\text{U}_4\text{O}_{32/3}$ (or $\text{U}_4\text{O}_{10.67}$) and a U_4O_9 cell would become $\text{U}_4\text{O}_{10.67}$ by the reaction of 1.67 (on the average) additional oxygen atoms. In the idealized development, there is a distinction between the oxygen in a lattice structure and the amount of additional oxygen in the lattice. For example, it is experimentally observed for spent fuel that the U_4O_9 crystallographic lattice structure has an additional ~ 0.6 oxygen atoms (i.e., it has a non-stoichiometric oxygen to uranium atomic (O/U) ratio of ~ 2.4). This excess atomic oxygen concentration has both kinematic and energetic dependences in the thermodynamic equations. Model development and additional experiments are necessary to clarify these dependences, and to address their impact on spent fuel performance in a repository environment.

REVIEW OF HOMOGENEOUS SPENT FUEL OXIDATION MODEL

Kinematics of Deformation

A model describing the deformation response of a contiguous set of lattice cells was developed.^[3] The model represented a lattice cell by a set of vector attributes. These vector attributes became the variables in density functions for the number of lattice cells of a particular species per unit volume. The lattice density was a stochastic function and species-dependent integrals over the set of vector attributes provide probable values for the deformation response. The deformation response was derived based on an idealized unit cell lattice

structure that has an effective height, width, and depth. At any time, attribute vectors denoted by $(\underline{a}, \underline{b}, \underline{c})$ can be assigned to describe the cell's dimensions, and in a reference configuration of deformation these vector attributes can be selected as a spatially local right-handed set of coordinates. A set of $(\underline{a}, \underline{b}, \underline{c})$ vector attributes can be assigned to every lattice cell in a spatial domain of volume R_0 enclosed by a boundary ∂R_0 . To represent a stochastic motion of deformation at time t , a set of velocity vector attributes $(\dot{\underline{a}}, \dot{\underline{b}}, \dot{\underline{c}})$ was also assigned to each lattice cell. Then, the probable number of cells at time t per unit spatial volume neighborhood of point $\underline{x}$ per unit vector attribute volume neighborhood of species point $(\underline{a}, \underline{b}, \underline{c}, \dot{\underline{a}}, \dot{\underline{b}}, \dot{\underline{c}})$ is denoted by a density function $P_{MN}(\underline{x}, t, \underline{a}, \underline{b}, \underline{c}, \dot{\underline{a}}, \dot{\underline{b}}, \dot{\underline{c}})$ where MN denotes a specific lattice phase. For shorthand purposes, the species space for the six vector attributes $\{\underline{a}, \underline{b}, \underline{c}, \dot{\underline{a}}, \dot{\underline{b}}, \dot{\underline{c}}\}$ was denoted as $\{q\}$, or domain Q ; i.e., lattice cell species q is an element in the lattice cell species domain Q . In order to identify and describe the evolution of different lattice structures for the three likely phases of UO_2 , three different density functions are defined: $P_{48}(\underline{x}, t, q)$ denotes the number density of U_4O_8 (i.e., UO_2) lattice cells such that each cell contains four uranium atoms, $P_{49}(\underline{x}, t, q)$ denotes the number density of U_4O_9 lattice cells such that each cell contains four uranium atoms, and $P_{38}(\underline{x}, t, q)$ denotes the number density of U_3O_8 (this phase will be denoted as U_3O_8 rather than $\text{U}_4\text{O}_{32/3}$) lattice cells such that each cell contains four uranium atoms, for point $\underline{x}$ in $R_0 + \partial R_0$ at time t .

The density functions P_{48} , P_{49} , and P_{38} can each be decomposed into two functions: one is for a "continuum-like" deformation response and the other is for a "discontinuum-like" deformation response. The decomposition functions are defined as $P_{48} \equiv P_{48}| + P_{48}]$, $P_{49} \equiv P_{49}| + P_{49}]$, $P_{38} \equiv P_{38}| + P_{38}]$, where the single bar symbol denotes the continuum response and the single square bracket denotes the discontinuum response. This decomposition is used to analytically represent the annihilation and creation rate changes in cell density when phase transformations occur. With respect to the deformation response description, the phase transformation from existing lattice cells to new cell sizes is represented as a discontinuum deformation because a lattice species q deforms

discontinuously into a species q^* that has finitely different dimensions within an arbitrarily small increment of time. Thus, a discontinuum lattice response contrasts to a continuum lattice response which has lattice species q deforming into a species q^* that has infinitesimally different dimensions within an arbitrarily small increment of time. In addition to lattice cell deformations, spent fuel contains fission product elements (including neutron reaction products (actinides)) that reside in interstitial and substitutional atomic lattice positions, vacancies (missing atoms), and for oxidation processes to occur, oxygen atoms; these four kinds of densities are aggregated and denoted by four density functions, P_I , P_S , P_V , and P_O , respectively. The function arguments of these four density functions are similar to the lattice density functions, except the deformation is incrementally discontinuous by incremental vector attributes ($\hat{a}$, $\hat{b}$, $\hat{c}$) as interstitial, substitutional, vacancy, and oxygen species migrate in and out of the lattice. Thus, their arguments are ($\underline{x}$, t , $\underline{a}$, $\underline{b}$, $\underline{c}$, $\hat{a}$, $\hat{b}$, $\hat{c}$, $\underline{v}_K$) where $\underline{x}$ is position, t is time, ($\underline{a}$, $\underline{b}$, $\underline{c}$) is the local lattice cell size, ($\hat{a}$, $\hat{b}$, $\hat{c}$) is the local incremental change in lattice vectors ($\underline{a}$, $\underline{b}$, $\underline{c}$) as a corresponding interstitial atom, substitutional atom, vacancy, or oxygen atom occupies a local position in a lattice cell, and $\underline{v}_K$ is the species velocity relative to the local lattice cell velocity ($K \sim I, S, V$, or O species). For shorthand, the previous set q vector attributes and space Q will be augmented with the attribute set ($\hat{a}$, $\hat{b}$, $\hat{c}$, $\underline{v}_K$) and all density functions will have the same arguments set; ($\underline{x}, t, q$).

Using the above definitions and lattice structure descriptors, a function for the deformation response of a material body can be developed in terms of lattice scale attributes. For this development consider two spatial points, say $\underline{x}_A$ and $\underline{x}_B$ in a material R_0 . To start, assume that the lattice cell structure is perfect and has only UO_2 lattices. Then, the probable total relative velocity $v\}_A^B$ of point B relative to point A at time t is

$$\begin{aligned} v\}_A^B = & \int_{\underline{x}_A}^{\underline{x}_B} \int_Q \left(\hat{a}_i e_{jkm} b_k c_m + \hat{b}_i e_{jkm} c_k a_m \right. \\ & \left. + \hat{c}_i e_{jkm} a_k b_m \right) P_{48}(\underline{\xi}, t, q) \\ & + \left(a_i e_{jkm} b_k c_m + b_i e_{jkm} c_k a_m + c_i e_{jkm} a_k b_m \right) \end{aligned}$$

$$\times \dot{\bar{P}}_{48}(\underline{\xi}, t, q) dq d\underline{\xi}_j \quad (2-1a)$$

which is the contribution to velocity from all lattice species (integration over Q) of volume elements (example, $d\underline{\xi}_j e_{jkm} b_k c_m$) along an arbitrary path from spatial point $\underline{x}_A$ to $\underline{x}_B$, where the total time rate of change for $\dot{\bar{P}}_{48}$ is defined as

$$\dot{\bar{P}}_{48} \equiv \partial_i P_{48} + \partial_i (v_i P_{48}) \quad (2-1b)$$

For notational shorthand purposes, equation (2-1a) can be written in terms of functional operators as

$$v\}_A^B \equiv \dot{L}_{ij48} P_{48} \Delta x_j\}_A^B + L_{ij48} \dot{\bar{P}}_{48} \Delta x_j\}_A^B \quad (2-2)$$

where the definitions for operators $\dot{L}_{ij48}(\cdot) \Delta x_j\}_A^B$ and $L_{ij48}(\cdot) \Delta x_j\}_A^B$ follow from equation (2-1a) and the $\Delta x_j\}_A^B$ is a shorthand for indicating spatial integration from point $\underline{x}_A$ to point $\underline{x}_B$.

To include relative lattice velocities from oxidation phase changes, the lattice density rates for functions P_{NM} are decomposed into continuum and discontinuum terms. In addition, the relative velocity of equation (2-2) for lattice motion is also dependent on oxygen, interstitial, substitutional, and vacancy density changes in the lattice cells along the line integral path between atoms A and B . As remarked previously, the incremental finite deformation is ($\hat{a}$, $\hat{b}$, $\hat{c}$), which is represented in the relative velocity with operator

$$\begin{aligned} L_{ijK}(\cdot) \equiv & \int_Q \left(\hat{a}_i e_{jkm} b_k c_m + \hat{b}_i e_{jkm} c_k a_m \right. \\ & \left. + \hat{c}_i e_{jkm} a_k b_m \right)_K (\cdot) dq \quad (2-3) \end{aligned}$$

where subscript K identifies the operator function as oxygen (O), interstitial (I), substitutional (S) and vacancy (V). Then, the relative velocity of equation (2-2) in an oxidizing UO_2 spent fuel lattice can be decomposed into continuum and discontinuum components that includes the added dependence on oxygen, interstitial, substitutional, and vacancy densities:

$$v\}_A^B = v\}_A^B + v\}_A^B \quad (2-4a)$$

$$v\}_A^B = \left(\dot{L}_{ij48} P_{48} + L_{ij48} \dot{\bar{P}}_{48} \right) \Delta x_j\}_A^B \quad (2-4b)$$

$$v_i\}_A^B = (L_{ij48} \dot{\bar{P}}_{48} + L_{ijK} \dot{\bar{P}}_K) \Delta x_j\}_A^B \quad (2-4c)$$

where continuum and discontinuum relative velocities $v_i|$ and $v_i]$ are defined in terms of the lattice cell decomposition functions $P_{48}|$ and $P_{48}]$ plus the K letter index for the four letters O, I, S, and V to obtain relative velocity contributions from oxygen, interstitial, substitutional, and vacancy density changes. The latter density functions have a time rate given by

$$\dot{\bar{P}}_K] \equiv \partial_t P_K] + \partial_i ((v_i + v_{Ki}) P_K]) \quad (2-4d)$$

The total velocity of position B is the velocity of position A plus the relative velocity, i.e.,

$$v_i(B, t) = v_i(A, t) + v_i\}_A^B \quad (2-4e)$$

where $v_i(A, t)$ is the velocity of position A with respect to an arbitrary frame of reference.

From equation (2-4), a relative deformation response can be written for the position of point B relative to point A by performing an integration over time. This integration requires an initial condition at $t=0$ (which is introduced by selecting a reference coordinate frame) and a time duration, say $t=0$ to $t=\Delta\tau$ where $\Delta\tau$ is an arbitrary future time. At time $\Delta\tau$ and for contiguous lattice cell species densities P_{MN} and point species $P_K]$, the total relative deformation of point B relative to point A, denoted by $\chi\}_A^B$, is given by

$$\chi_i\}_A^B = X_i\}_A^B + \int_0^{\Delta\tau} v_i\}_A^B d\tau \quad (2-5a)$$

$$= X_i\}_A^B + (L_{ijMN} P_{MN}| + L_{ijMN} \dot{\bar{P}}_{MN}| + L_{ijMN} \dot{\bar{P}}_{MN}] + L_{ijK} \dot{\bar{P}}_K]) \Delta x_j\}_A^B \Delta\tau \quad (2-5b)$$

where the $L_{ijMN}(\cdot) \Delta x_j] \Delta\tau$ and $L_{ijK}(\cdot) \Delta x_j] \Delta\tau$ functional operators include a $\Delta\tau$ to denote integration over time, as indicated in equation (2-5a), and $X\}_A^B$ is the initial position vector of point B relative to point A at time $t = 0$. In equation (2-5b), the total relative deformation is decomposed into continuum and discontinuum functionals, which are defined over independent function spaces containing $P_{MN}|$, $P_{MN}]$ and $P_K]$. For the thermodynamic model of the next section, a strain

tensor derived from only the continuum part of the deformation is used as a thermodynamic function argument, and it can be shown to be given by (see [4-5] for analog derivations)

$$2\gamma_{ij}| = (\dot{L}_{ijMN} + \dot{L}_{jiMN}) P_{MN}| \Delta\tau + (L_{ijMN} + L_{jiMN}) \times \dot{\bar{P}}_{MN}| \Delta\tau + \text{second order terms} \quad (2-6a)$$

$$= (L_{ijMN} + L_{jiMN}) (P_{MN}(\underline{x}, t, q)| - P_{MN}(\underline{x}, o, q_o)|) \quad (2-6b)$$

where equation (2-6b) is a time integration of the total time derivative of $(L_{ijMN} P_{MN}|)$ over the time interval (o, t) to give a time integrable strain measure relative to an idealized "unstrained" reference lattice cell set $\{q_o\}$ that is continuum-like for each phase MN. For the present analysis, only the linear terms of $P_{MN}|$ and $\dot{\bar{P}}_{MN}|$ will be retained, then the gradient of the continuum relative velocity of equation (2-4b) will be equal to the time derivative of the linear strain tensor in equation (2-6). This completes a review of kinematic measures for lattice deformations that will be used in the following section on thermodynamic modelling.

Energetics of Homogeneous Phase Transformation Thermodynamics

A nonequilibrium thermodynamic model will be reviewed for the rate of entropy production during homogeneous oxidation phase transformations of spent fuel.[3] The model represented the internal energy change terms that arise from the stress-strain work for a deforming lattice structure, mass transport, and from phase transformation energies between homogeneous lattice structures. From the entropy rate response and an Onsager thermodynamic formulation,[6] an oxidation response functional was written that expressed the kinetics of phase changes as functionally dependent on the thermodynamic force for transport and the thermodynamic force for phase change energetics. This representation was for a spatially continuous phase change process. Additional analysis will be completed in a later section to extend the following thermodynamic expressions to address a phase change front that propagates as a spatial surface of discontinuity between two phases.

To begin this review, assume that an internal energy functional, $\bar{\epsilon}$, exists (energy per unit spatial volume) that has function arguments of entropy $\eta(\underline{x}, t)$, continuum strain $\underline{\gamma}(\underline{x}, t)$, the three lattice phase density functions $P_{48}(\underline{x}, t, q)$, $P_{49}(\underline{x}, t, q)$, $P_{38}(\underline{x}, t, q)$, and the four point density functions for atom and vacancy density concentrations, $P_O(\underline{x}, t, q)$, $P_I(\underline{x}, t, q)$, $P_S(\underline{x}, t, q)$, $P_V(\underline{x}, t, q)$;

$$\bar{\epsilon}(\underline{x}, t) = \epsilon(\eta, \underline{\gamma}, P_{48}, P_{49}, P_{38},$$

$$P_O, P_I, P_S, P_V)$$

$$\equiv \epsilon(f) \quad (3-1)$$

where f is shorthand to replace the writing of the nine functions. The spatial domain of points $\underline{x}$ is $R_0 + \partial R_0$, the species domain of q is $\{q\}$ or Q , and the time domain is time t greater than an initial time at $t=0$. In addition to an existence of ϵ , a functional form will be assumed for the internal energy in terms of functional operators that effectively integrate out the explicit dependence of the variables q in ϵ to obtain $\bar{\epsilon}(\underline{x}, t)$. This energy functional form is an analytical equivalent of the physical problem of having a space domain $R_0 + \partial R_0$ at time t filled with various possible compositions of lattice densities of type P_{48} , P_{49} , and P_{38} , with their associated energies, and into which oxygen atoms, interstitial atoms, substitutional atoms, and vacancies defect densities of P_O , P_I , P_S , P_V , respectively, are inserted with their associated energies. This can be written as

$$\begin{aligned} \bar{\epsilon}(\underline{x}, t) = \epsilon(f) \equiv & \Delta P_{48} \epsilon(f) P_{48}] \\ & + \Delta P_{49} \epsilon(f) P_{49}] + \Delta P_{38} \epsilon(f) P_{38}] \\ & + \Delta P_O \epsilon(f) P_O] + \Delta P_I \epsilon(f) P_I] \\ & + \Delta P_S \epsilon(f) P_S] + \Delta P_V \epsilon(f) P_V] \end{aligned} \quad (3-2)$$

where the $\Delta(\cdot)\epsilon$ denote thermodynamic chemical potential energies that are functional operators (integrates over domain Q) defined from the internal energy functional. Note that the above is an analytical statement that the internal energy at a point and time is the energy of the lattice species plus the energy of the atoms/vacancies added to that lattice. Also, note that the above energy expression does not explicitly represent any oxide

and other compounds plus metal alloy clusters that may form within the aggregate set of fission product elements. However, if such oxides/compounds in spent fuel exist before and after a uranium oxidation phase transformation, then their energy change effect on the kinetics of the uranium phase transformation would not be an explicit net energy term in an energy change rate expression. Thus, while equation (3-2) represents a physical view of lattice plus atom/vacancy energy contributions to the internal energy functional, it also illustrates a significant lack of detailed knowledge of the fission product sub-energies that exist within the possible uranium oxide phases of spent fuel. This lack of detailed knowledge can only be augmented and completed by experimental methods; however, for spent fuel oxidation response within the expected environmental time-histories of geological repositories, the above internal energy assumption represents an initial starting point in model development that also may be sufficient. Using repeated subscripts, equation (3-2) is written

$$\epsilon(f) = \Delta P_{NM} \epsilon P_{NM}] + \Delta P_K \epsilon P_K] \quad (3-3)$$

where the repeated subscript (NM) denotes a sum over the four lattice density functions and the repeated subscript (K) denotes a sum over the three atomic and the vacancy functions.

For quasi-static deformation processes (no kinetic energy/acceleration terms) in spatial domains that do not have a propagating surface of discontinuity, the first law of thermodynamics sets the rate of change of internal energy equal to the rate of work (body force plus stress), $\dot{\bar{W}}$, plus the rate of heat change, $\dot{\bar{H}}$, for any spatial subset $R + \partial R$ in $R_0 + \partial R_0$,

$$\dot{\bar{\epsilon}} = \dot{\bar{W}} + \dot{\bar{H}} \quad (3-4)$$

The rate of heat exchange for spatial domain $R + \partial R$ is

$$\dot{\bar{H}} = \int_R \dot{H}_o d\underline{x} + \int_{\partial R} h_i n_i d\underline{x} \quad (3-5)$$

where $\dot{H}_o$ is the heat generation rate at points in R and h_i is the heat flux vector at points on boundary ∂R , and n_i is the outward directional unit normal vector at points on boundary ∂R . The rate of work on spatial domain $R + \partial R$ is

$$\dot{\bar{W}} = \int_R f_j v_j d\mathbf{x} + \int_{\partial R} \sigma_{ij} n_i v_j d\mathbf{x} \quad (3-6)$$

where f_i is the body force vector, v_i is the velocity vector, and σ_{ij} is the stress tensor. The rate of internal energy change for the spatial domain $R + \partial R$ is

$$\begin{aligned} \dot{\bar{E}} = & \int_R \partial_t \varepsilon(f) d\mathbf{x} + \int_{\partial R} \varepsilon(f) v_i n_i \\ & + \Delta_{P_K} \varepsilon(f) P_K \big] v_{K_i} n_i d\mathbf{x} \end{aligned} \quad (3-7)$$

where the first integral is the time rate of change of internal energy at spatial points in R and the second integral is the flux of internal energy through boundary ∂R at the local velocity of the lattice ($v_i n_i$) plus the flux of internal energy from the oxygen, interstitial, substitutional, and vacancies density functions at their relative velocity ($v_K \cdot n$) with respect to the lattice velocity v_i . The surface integral expression in equations (3-5), (3-6), and (3-7) over ∂R can be rewritten as volume integrals by applying the divergence theorem of integral calculus, providing that the integrands are spatially continuous functions within domain R . This is the assumed case for the present analysis. Therefore, equations (3-5), (3-6), and (3-7) can be substituted into equation (3-4) from which, along with the velocity expression of section 2 and the use of the divergence theorem, one obtains the following form of equation (3-4) as a volume integral over R :

$$\begin{aligned} & \int_R (\Delta_\eta \varepsilon \dot{\eta} - \dot{H}_o - \partial_i h_i) d\mathbf{x} \\ & = \int_R \left((f_j + \partial_i \sigma_{ij}) \cdot v_j + \sigma_{ij} \partial_i v_j - \Delta_{\gamma_{ij}} \varepsilon \dot{\gamma}_{ij} \right. \\ & \quad \left. - \Delta_{P_{NM}} \varepsilon \dot{\bar{P}}_{NM} \right] - \Delta_{P_K} \varepsilon \dot{\bar{P}}_K \big] \\ & \quad \left. - \partial_i (\Delta_{P_K} \varepsilon) P_K \big] v_{K_i} \right) d\mathbf{x} \end{aligned} \quad (3-8)$$

The term on the left side of equation (3-8) is the total entropy rate energy minus heat; this net energy rate is the rate of entropy dissipation/production energy; and will be denoted here by

$\Delta_\eta \varepsilon \dot{\eta}^*$. For nonequilibrium thermodynamic processes, the entropy dissipation rate is non-negative. The first term on the right side of equation (3-8) contains the stress equilibrium

expression, which must be zero because the velocity is arbitrary, hence

$$f_j + \partial_i \sigma_{ij} = 0 \text{ for all } \mathbf{x} \text{ in } R \quad (3-9)$$

The remaining terms in equation (3-8) are internal energy rates associated with the stress-velocity gradient work rate, strain energy rate, phase transformation rates, and mass transport rates. Using the above entropy dissipation/production function, η^* , equations (2-4b), (2-6), and (3-9), and the assumptions of small continuum strains

(i.e., neglect higher order strain terms in $\dot{\gamma}_{ij}$), equation (3-8) can be written as

$$\begin{aligned} \int_R \Delta_\eta \varepsilon \dot{\eta}^* d\mathbf{x} = & \int_R \left((\sigma_{ij} - \Delta_{\gamma_{ij}} \varepsilon) \dot{\gamma}_{ij} \right. \\ & \left. + \sigma_{ij} L_{ij_{NM}} \dot{\bar{P}}_{NM} \right] + \sigma_{ij} L_{ij_K} \dot{\bar{P}}_K \big] \\ & - \Delta_{P_{NM}} \varepsilon \dot{\bar{P}}_{NM} \big] - \Delta_{P_K} \varepsilon \dot{\bar{P}}_K \big] \\ & - \partial_i (\Delta_{P_K} \varepsilon) P_K \big] v_{K_i} \big] d\mathbf{x} \end{aligned} \quad (3-10)$$

In equation (3-10), the rate of entropy production energy has four generic possible energy rate contributions, the sum of which must not be non-negative. The energy rate contributions have thermodynamic processes identified with strain rate

processes $\dot{\gamma}_{ij}$, lattice-phase change rate processes $\dot{\bar{P}}_{NM}$, atom/vacancy density rate change process $\dot{\bar{P}}_K$, and atom/vacancy density flux processes $P_K \big] v_{K_i}$. In this analysis, as well as the following surface of discontinuity analysis, all continuum strain rate processes are assumed to occur at thermodynamic equilibrium, hence

$$\sigma_{ij} = \Delta_{\gamma_{ij}} \varepsilon \quad (3-11)$$

and this eliminates the strain rate term in equation (3-10). More importantly, this assumption also means, for modeling purposes here, that all homogeneous phase change kinetic processes are kinematically accessible; i.e., the deformed configuration of a possible phase transformation is not constrained by any prescribed displacement/traction boundary conditions. This assumption does not require that phase transformations occur at zero stress. In fact, the stress state for the U_4O_8 to U_4O_9 transformation is

sufficient to form microcracks, and for the U_4O_9 to U_3O_8 transformation, particles will increase in volume by approximately 30%, which could result in stresses sufficient to form a flaked powder material.

Returning to equation (3-10), consider a possible sequence of oxidation phase of U_4O_8 to U_4O_9 to U_3O_8 for a volume of spent fuel in an arbitrary spatial domain R . To transform from U_4O_8 to only U_4O_9 , the lattice rates $\dot{\bar{P}}_{48}$ and $\dot{\bar{P}}_{49}$ are the only non-zero lattice rates. In addition, the interstitial oxygen atomic density in the idealized lattice of U_4O_8 has a discontinuous transition in density as the U_4O_9 lattice phase is formed during the transformation from U_4O_8 to U_4O_9 . As per the discussion of volumes in a previous section, each volume of a created U_4O_9 lattice, with its four uranium atoms of the P_{49} lattice, will remove a U_4O_8 lattice volume containing four uranium atoms and one oxygen atom of the P_O oxygen density form a U_4O_9 lattice; i.e.,

The mass balance for this phase transformation can also be expressed in terms of rates of change in the lattice density functions P_{48} and P_{49} , and the oxygen density function P_O relative to the two different lattices as

$$\dot{\bar{P}}_{49} \Leftrightarrow -\dot{\bar{P}}_{48}; \quad (3-13a)$$

$$\dot{\bar{P}}_{49} \Leftrightarrow -\dot{\bar{P}}_{O48} - \dot{\bar{P}}_{O49} \quad (3-13b)$$

where (3-13a) functionally expresses a removal rate of U_4O_8 lattice (four UO_2 lattices) at the rate one U_4O_9 lattice is formed and (3-13b) functionally expresses the $\dot{\bar{P}}_{O48}$ removal rate of all oxygen from the U_4O_8 lattice, such that a $\dot{\bar{P}}_{O49}$ rate becomes interstitial oxygen in the U_4O_9 lattice and the rest is consumed at a rate equal to the $\dot{\bar{P}}_{49}$ rate at which the U_4O_9 lattice is formed. In addition to the above two functional conservation expressions, analogous ones are assumed to exist for the interstitial, substitutional, and vacancy density functions as the U_4O_8 lattice transforms to a U_4O_9 lattice, i.e.,

$$\dot{\bar{P}}_{I49} \Leftrightarrow -\dot{\bar{P}}_{I48}; \quad \dot{\bar{P}}_{S49} \Leftrightarrow -\dot{\bar{P}}_{S48};$$

$$\dot{\bar{P}}_{V49} \Leftrightarrow -\dot{\bar{P}}_{V48} \quad (3-13c)$$

Substituting equation (3-11) and expressions (3-13) into equation (3-10), and considering only the U_4O_8 to U_4O_9 transformation, the dissipation entropy energy rate can be written as

$$\begin{aligned} \int_R \Delta_{\eta} \epsilon \dot{\eta}^* \Big|_{48}^{49} d\mathbf{x} = & \int_R \left(\left(\sigma_{ij} L_{ij} \Big|_{48}^{49} \right. \right. \\ & - \left. \sigma_{ij} L_{ijo} \Big|_{48}^{49} + \Delta_{P_{48}} \epsilon + \Delta_{P_O} \epsilon - \Delta_{P_{49}} \epsilon \right) \dot{\bar{P}}_{49} \\ & + \left(\sigma_{ij} L_{ijo} \Big|_{48}^{49} - \Delta_{P_O} \epsilon \Big|_{48}^{49} \right) \dot{\bar{P}}_{O49} \\ & + \left(\sigma_{ij} L_{ijl} \Big|_{48}^{49} - \Delta_{P_I} \epsilon \Big|_{48}^{49} \right) \dot{\bar{P}}_{I49} \\ & + \left(\sigma_{ij} L_{ijs} \Big|_{48}^{49} - \Delta_{P_S} \epsilon \Big|_{48}^{49} \right) \dot{\bar{P}}_{S49} \\ & + \left(\sigma_{ij} L_{ijv} \Big|_{48}^{49} - \Delta_{P_V} \epsilon \Big|_{48}^{49} \right) \dot{\bar{P}}_{V49} \\ & - \partial_i \left(\Delta_{P_K} \epsilon \right) P_K \Big|_{48}^{49} v_{Ki} d\mathbf{x} \end{aligned} \quad (3-14)$$

where terms such as $\sigma_{ij} L_{ij} \Big|_{48}^{49}$ operating on $\dot{\bar{P}}_{49}$ is shorthand notation for the stress work during the U_4O_8 to U_4O_9 transformation, $(\sigma_{ij} L_{ij49} - \sigma_{ij} L_{ij48}) \times \dot{\bar{P}}_{49}$ (the second term results from expression [3-13a]), and terms such as $\Delta_{P_S} \epsilon \Big|_{48}^{49}$ operating on $\dot{\bar{P}}_{S49}$ denote the internal energy changes for substitutional atoms in the U_4O_9 lattice relative to the U_4O_8 lattice, $(\Delta_{P_S} \epsilon_{49} \dot{\bar{P}}_{S49} - \Delta_{P_S} \epsilon_{48} \dot{\bar{P}}_{S49})$ (the second term results from expression (3-13c)). From equation (3-14), the dissipation entropy rate for U_4O_8 transforming to U_4O_9 depends on energy terms from the rate of five density functions and four flux density functions. Note that if equation (3-14) were applied to an ideally perfect sample of U_4O_8 , i.e., no fission products ($P_S = P_I = 0$) and stoichiometric phase transformations, then only the rate $\dot{\bar{P}}_{49}$ and the flux $P_O v_{Oi}$ term would be present as possible terms that contribute entropy energy. Thus, equation (3-14) addresses the

additional energies, in an aggregate and phenomenological modelling analysis, that occur as U_4O_8 spent fuel transforms to a U_4O_9 lattice with non-zero values for P_V , P_S , and P_I densities.

After the U_4O_9 lattice phase is attained, current spent fuel experiments show a O/U of ~ 2.4 (U_4O_9 ideally is O/U of 2.25), thus there exists an excess O/U of ~ 0.15 , hence, excess oxygen in the U_4O_9 lattice. Atomistically, this amount of oxygen is more than sufficient to create a U_3O_7 (U_3O_7 ideally is O/U of 2.33) phase; however, a U_3O_7 lattice phase has not been observed in the samples from existing low temperature spent fuel oxidation experiments. Thus, the spent fuel U_4O_9 phase is a metastable energy phase relative to U_3O_7 . Equation (3-14) could be readily modified to represent the entropy rate for a U_4O_9 to U_3O_7 phase transformation by replacing the previous "48" by "49", the previous "49" by "37" and minor changes in numerical coefficients (analogous to expression (3.13)). This development will not be treated here.

The next expected spent fuel phase is U_3O_8 , which will require additional oxygen to be transported into the U_4O_9 lattice for the transformation to occur. At the present time, there is uncertainty about the path to U_3O_8 ; i.e., does U_3O_8 form with the addition of sufficient oxygen directly from the nonstoichiometric U_4O_9 lattice, or is there an intermediate temporary phase; perhaps U_3O_7 and then to U_3O_8 . Because U_3O_7 is a stoichiometric accessible phase from the U_4O_9 lattice with a O/U of ~ 2.4 , its potential intermediate existence will be neglected and equation (3-14) rewritten to represent the thermodynamic energy rates for a transformation directly from U_4O_9 lattice to the U_3O_8 lattice. This is done by changing in equation (3-14) the existing "48" to "49" and the previous "49" to "38"; and the numerical coefficients to satisfy lattice-mass balance relationships are given by the following functional expressions:

$$\begin{aligned}\dot{\bar{P}}_{38}] &\Leftrightarrow -\dot{\bar{P}}_{49}]; \quad \dot{\bar{P}}_{V38} \Leftrightarrow -\dot{\bar{P}}_{V49} \\ \dot{\bar{P}}_{38}] &\Leftrightarrow -\dot{\bar{P}}_{O49} - \dot{\bar{P}}_{O38} \\ \dot{\bar{P}}_{I38} &\Leftrightarrow -\dot{\bar{P}}_{I49}; \quad \dot{\bar{P}}_{S38} \Leftrightarrow -\dot{\bar{P}}_{S49} \quad (3-15)\end{aligned}$$

Then the thermodynamics for the entropy energy rate of U_4O_9 to U_3O_8 transformations is:

$$\begin{aligned}\int_R \Delta_\eta \epsilon \dot{\eta}^*]_{49}^{38} d\mathbf{x} &= \int_R \left(\left(\sigma_{ij} L_{ij} \right]_{49}^{38} - \sigma_{ij} L_{ijo} \right]_{49}^{38} \\ &+ \Delta_{P_{48}} \epsilon + \Delta_{P_0} \epsilon - \Delta_{P_{38}} \epsilon \Big) \dot{\bar{P}}_{38}] \\ &+ \left(\left(\sigma_{ij} L_{ijo} \right]_{49}^{38} - \Delta_{P_0} \epsilon \right]_{49}^{38} \Big) \dot{\bar{P}}_{O38}] \\ &+ \left(\left(\sigma_{ij} L_{ijl} \right]_{49}^{38} - \Delta_{P_I} \epsilon \right]_{49}^{38} \Big) \dot{\bar{P}}_{I38}] \\ &+ \left(\left(\sigma_{ij} L_{ijs} \right]_{49}^{38} - \Delta_{P_S} \epsilon \right]_{49}^{38} \Big) \dot{\bar{P}}_{S38}] \\ &+ \left(\left(\sigma_{ij} L_{ijv} \right]_{49}^{38} - \Delta_{P_V} \epsilon \right]_{49}^{38} \Big) \dot{\bar{P}}_{V38}] \\ &- \partial_i \left(\Delta_{P_K} \epsilon \right) P_K] v_{Ki} \Big) d\mathbf{x} \quad (3-16)\end{aligned}$$

For homogeneous phase transformations, the full nonequilibrium thermodynamic rate response model from equation (3-16) would couple functionally the nine rate flux functions ($\dot{\bar{P}}_{38}]$, $\dot{\bar{P}}_{O38}]$, $\dot{\bar{P}}_{I38}]$, $\dot{\bar{P}}_{S38}]$, $\dot{\bar{P}}_{V38}]$, $P_O]v_{O_i}$, $P_I]v_{I_i}$, $P_S]v_{S_i}$, $P_V]v_{V_i}$) with their conjugate functional operators (coefficients) in equation (3-16) in a nine-by-nine matrix (counting the four vector fluxes as vector equations, it would be tensorially a 21 by 21 matrix). This type of model was developed in reference [3] for the simplified case of homogeneous phase transformations. The nonequilibrium rate equations for the spatially inhomogeneous phase transformation problem will be developed in the following section. The phase transformation equations are first derived across propagating surfaces which separate different uranium oxide crystallographic lattice structures.

INHOMOGENEOUS OXIDATION PHASE TRANSFORMATIONS

Kinematics and Energetics Across a Propagating Phase Front

In the previous review sections, the spatial dependence of the density functions P_{MN} and P_K were assumed to be continuous. In this section these density functions are assumed to be spatially discontinuous. The discontinuity for the functions is taken to be across an idealized smooth surface $\partial R]$ in the spatial domain $R_0 + \partial R_0$. For the U_4O_8 to U_4O_9 phase transformation, the surface is denoted as $\partial R]_{48}^{49}$ and the U_4O_9 to U_3O_8 phase surface is denoted as $\partial R]_{49}^{38}$. Let surface $\partial R]_{48}^{49}$ have a propagation velocity denoted by $\underline{V}_{48}$ and surface $\partial R]_{49}^{38}$ have a propagation velocity denoted by $\underline{V}_{49}$.

Consider first an arbitrary subdomain $R + \partial R$ of $R_0 + \partial R_0$ that contains a propagating discontinuity surface $\partial R]_{48}^{49}$. It follows that in $R + \partial R$, lattice structures of U_4O_8 and U_4O_9 exist, and are instantaneously separated by surface $\partial R]_{48}^{49}$. In domain $R + \partial R$, consider the additive existence of density functions $P_{48}]$ and $P_{49}]$; and their time rates of change. For the case of no discontinuity surface $\partial R]_{48}^{49}$, for any arbitrary time t , the result is

$$\int_R \partial_t (P_{48}] + P_{49}]) dR + \int_{\partial R} (P_{48}] + P_{49}]) \underline{v}_i n_i d(\partial R) = 0 \quad (4-1)$$

which follows because each four uranium atoms occupy a lattice and the lattice is either U_4O_8 or U_4O_9 . Next, consider the case where $R + \partial R$ contains surface $\partial R]$ with unit normal vector $\underline{n}$ propagating at velocity $\underline{V}_{48}$ into a U_4O_8 spatial domain, then equation (4-1) still must equal zero, but it will contain additional terms for $\partial R]$, i.e.

$$\int_R \partial_t (P_{48}] + P_{49}]) dR + \int_{\partial R} (P_{48}] + P_{49}]) \underline{v}_i n_i d(\partial R)$$

$$+ \int_{\partial R]^+} (P_{48}] + P_{49}]) (\underline{v}_i^+ - V_{i48}) n_i^+ d(\partial R]) + \int_{\partial R]^-} (P_{48}] + P_{49}]) (\underline{v}_i^- - V_{i48}) n_i^- d(\partial R]) = 0 \quad (4-2)$$

where the (+) and (-) superscripts denote opposite sides of the surface $\partial R]$. Because the front $\partial R]$ divides $R + \partial R$ into subdomains of only U_4O_8 or U_4O_9 , then equation (4-1) can be used to reduce equation (4-2) to a surface integral condition (jump condition) only on $\partial R]$ that is equal to zero; and can be written as

$$\int_{\partial R]} (P_{48}] + P_{49}]) (\underline{v}_i - V_{i48}) n_i d(\partial R]) = 0 \quad (4-3)$$

where n_i is directed parallel to n_i^+ and the bold bracket $(\])^+$ is a shorthand notation for combining the difference of the integrand on opposites of the front $\partial R]$. Finally, since the domain $R + \partial R$ was arbitrary in extend, it follows that the integrand of equation (4-3) is zero at all points along $\partial R]$; hence, the pointwise difference condition along $\partial R]$ in $R_0 + \partial R_0$ is

$$(P_{48}] + P_{49}]) (\underline{v}_i - V_{i48}) n_i = 0 \text{ for } \underline{x} \text{ on } \partial R] \quad (4-4a)$$

which appears as a standard shock front discontinuity condition across a propagating surface. For the conditions defined above, the surface $\partial R]$ moves into the U_4O_8 spatial domain at velocity V_{i48} and n_i points outward (positive) from the U_4O_9 domain; thus, equation (4-4a) can be written as

$$(P_{48}^+]) (\underline{v}_i^+ - V_{i48}) - P_{49}^-]) (\underline{v}_i^- - V_{i48}) n_i = 0 \quad (4-4b)$$

because $P_{49}^+]$ is zero on the U_4O_8 side of surface $\partial R]$ and $P_{48}^-]$ is zero on the U_4O_9 side of surface $\partial R]$. For the case of $\underline{v}_i^+$ equal to zero (the U_4O_8 lattice fixed), equation (4-4b) can be expressed as the number of $P_{49}^-]$ lattices in terms of the number of $P_{49}^+]$ per unit spatial volume across $\partial R]$ as

$$P_{49}^-] = -P_{48}^+]) (V_{j48} n_j / (-\underline{v}_i^+ - V_{i48}) n_i) \quad (4-4c)$$

where $v_i\}^+_-$ is the discontinuity in lattice velocity across the propagating phase front ∂R . Physically, the velocity fraction term in equation (4-4c) is the volume change across the phase front to correctly evaluate the number of lattice cells per unit spatial volume. In the case of a U_4O_8 transformation to U_4O_9 , the stress-free lattice dimensions decrease, and the relative velocity $v_i\}^+_-$ n_i is negative across ∂R for the normal vector n_i directed from the U_4O_9 side into the U_4O_8 side. Thus, there are more P_{49} lattice cells per unit spatial volume than there were P_{48} lattice cells per unit spatial volume created as the oxidation front propagates into the U_4O_8 spatial domain.

An analysis similar to that completed for lattice densities across a front ∂R can also be done for the atom/vacancy densities P_K . However, each density function of the set P_K can have a singular gain/loss representation across a oxidation front; in particular, consider the atomic oxygen density P_O which must change as U_4O_8 takes a lattice oxygen atom to create U_4O_9 . Thus, the analog of equation (4-3) for the P_K

$$\begin{aligned} & \int_{\partial R} P_K \left[(v_i + v_{K_i} - V_{i48}) \right]^+_- n_i d(\partial R) \\ &= - \int_{\partial R} \dot{p}_K \left[n_i \right]^+_- n_i d(\partial R) \end{aligned} \quad (4-5a)$$

where

$$\dot{p}_K \left[n_i \right]^+_- n_i = \dot{p}_K^+ n_i^+ n_i - \dot{p}_K^- n_i^- n_i \quad (4-5b)$$

and since $n_i^+ n_i = -1$ and $n_i^- n_i = +1$ for the unit normal vector for n_i directed from the R^- (U_4O_9) subdomain. The two-sided gain/lost rate terms provide a means of addressing the lattice source of the species, $\dot{p}_K^+$ from R^+ and $\dot{p}_K^-$ from R^- sides of ∂R . For example, the oxygen atoms for U_4O_8 to U_4O_9 conversion can be from the excess lattice oxygen atoms in the U_4O_9 lattice (R^- side of ∂R) or from those in the U_4O_8 lattice (R^+ side of ∂R) or a combination thereof. The lattice source of oxygen atoms is partly determined by the solid-state solubility limit of oxygen atoms in the lattice structure, and this will affect the energetics of the oxidation process. Finally, regardless of the source, for each U_4O_9 lattice created from a U_4O_8

lattice, one oxygen atom is required for stoichiometric U_4O_9 ; and additional oxygen atoms are required for hyper-stoichiometric U_4O_9 lattice with an O to U ratio of ~ 2.4 . Thus, there is a net positive flux of oxygen atoms to ∂R , which must equal $\dot{p}_O^+ + \dot{p}_O^-$ on ∂R . For the case of non-stoichiometric U_4O_9 with an oxygen to uranium ratio of ~ 2.4 , the sum of $\dot{p}_O^+$ and $\dot{p}_O^-$ must be about 1.6 oxygen atoms per unit crystal lattice site of U_4O_8 transformed into a lattice site of U_4O_9 . For a species density "K" which has zero net flux to surface ∂R , then the terms $\dot{p}_K^+$ and $\dot{p}_K^-$ are each assumed to be zero.

From equation (4-5a), and because surface segment ∂R is part of an arbitrary subdomain $R + \partial R$ in $R_0 + \partial R_0$, the pointwise form across surface ∂R is

$$\begin{aligned} & \left(P_K^+ \left[(v_i^+ + v_{K_i}^+ - V_{i48}) + \dot{p}_K^+ \right] n_i^+ \right. \\ & \left. = P_K^- \left[(v_i^- + v_{K_i}^- - V_{i48}) - \dot{p}_K^- \right] n_i^- \right) \end{aligned} \quad (4-6a)$$

For the case of stationary U_4O_8 ($v_i^+ = 0$), the equation (4-6a) can be solved for the flux of species "K" from the U_4O_9 , or R^- side, to ∂R , which is

$$\begin{aligned} & P_K^- \left[(v_i^- + v_{K_i}^- - V_{i48}) n_i \right. \\ & \left. = \left(P_K^+ \left[(v_{K_i}^+ - V_{i48}) + \dot{p}_K^+ \right] n_i \right) n_i \right) \end{aligned} \quad (4-6b)$$

or this can also be written as

$$\begin{aligned} & P_K^- \left[(v_i^- + V_{i48}) n_i = P_K^+ \left[V_{i48} n_i \right. \right. \\ & \left. \left. + \left(P_K^- v_{K_i} + \dot{p}_K^- \right) n_i \right] \right]^+_- n_i \end{aligned} \quad (4-6c)$$

Equation (4-6c) is the form that is believed most useful in developing a nonequilibrium thermodynamic response.

The relative velocity $v_i\}^+_-$ across ∂R can be evaluated with equation (2-4) and the reference elasticity strain measured introduced in equation (2-6) from the following expression;

$$v_i\}^+_- = \int_{\underline{x}^-}^{\underline{x}^+} \frac{L_{ijNM}(P_{NM}| - P_{NMO})}{L_{ijNM}(P_{NM}| - P_{NMO})} + L_{ijNM} \dot{\bar{P}}_{NM} + L_{ijK} \dot{\bar{P}}_K] dx_j \quad (4-7)$$

where $P_{NMO}|$ is $P_{NM}(\underline{x}, 0, q_0)$ and $\underline{x}^+$ is on the U_4O_8 side of ∂R and $\underline{x}^-$ is on the U_4O_9 side of ∂R . Equation (4-7) is for a relative velocity measure, hence, the integration can be performed moving with the phase front velocity V_{j48} to obtain a lattice discontinuity velocity across ∂R of

$$v_i\}^+_- = L_{ijNM}(P_{NM}| - P_{NMO})(v_j - V_{j48})^+_- + L_{ijNM} P_{NM}(v_j - V_{j48})^+_- + L_{ijK} P_K(v_j + v_{Kj} - V_{j48})^+_- \quad (4-8)$$

For the case of a U_4O_9 oxidation phase front propagating into a stationary U_4O_8 phase, ($v_j^+ = 0$), equation (4-8) becomes (plus side is U_4O_8 and minus side is U_4O_9)

$$v_i\}^+_- = -L_{ij48}(P_{48}^+| - P_{48O}^+)(V_{j48}) - L_{ij49}(P_{49}^-| - P_{49O}^-)(-v_j\}^+_- - V_{j48}) - L_{ij48} P_{48}^+(V_{j48}) - L_{ij49} P_{49}^-(-v_j\}^+_- - V_{j48}) + L_{ijK} P_K^+(v_{Kj}^+ - V_{j48}) - L_{ijK} P_K^-(-v_j\}^+_- + v_{Kj}^- - V_{j48}) \quad (4-9)$$

where the velocity v_j^- on the minus side (U_4O_9) of the front ∂R has been replaced with $-v_i\}^+_-$ for a stationary U_4O_8 phase ($v_j^+ = 0$) on the plus side of the front ∂R . Note that $v_i\}^+_-$ is not explicitly evaluated in equation (4-9) since it exists on both sides of the equal sign. Furthermore, the total relative velocity does not decompose in simple "continuum" and "discontinuum" terms in the

general tensor form given in equation (4-9). However, results from equations (4-4) through (4-6) can be combined into equation (4-9); which along with the physically reasonable assumption that the crystallographical lattice vectors are narrowly distributed about their corresponding lattice dimensional sizes for $UO_2(U_4O_9)$ and U_4O_9 (i.e., functions $P_{NM}|$ and P_{NM} are independent, and the P_{NM} and P_K density functions are mathematically represented by Dirac delta functions about their corresponding lattice dimensional vectors on vector domains $\{\underline{a}, \underline{b}, \underline{c}\}$) can be used to reduce equation (4-9) to the form

$$v_i\}^+_- = -v_i\}^+_{48} = L_{ijNM}^{48} P_{48}^+|_0 V_{j48} + L_{ijNM}^{48} P_{48}^+ V_{j48} + L_{ijK}^{48} (P_K^+ (v_{Kj}^+ - V_{j48}) + \dot{P}_K] n_j)^{48} \quad (4-10)$$

where

$$L_{ijNM}^{48} \equiv L_{ij49}(q_{49}) - L_{ij48}(q_{48}) \quad (4-11a)$$

$$P_{NM}^+|_0 \equiv P_{NM}(\underline{x}^+, t, q_{NM}) \quad (4-11b)$$

$$- P_{NM}(\underline{x}^+, 0, q_{NM})$$

$$L_{ijK}^{48} \equiv L_{ijK}(q_{49}) - L_{ijK}(q_{48})$$

and the argument (q_{NM}) denotes that the operators L_{ijNM} and L_{ijK} , and the density function (Dirac delta functions) are evaluated at the "NM" lattice vector values of $(\underline{a}, \underline{b}, \underline{c})$. Physically, equation (4-10) is an explicit representation for the velocity discontinuity across propagating oxidation front. This relative velocity has three contributions; the first is the continuum term and results from the elastic strain changes across ∂R which are small compared to lattice vector changes for a U_4O_8 phase change to U_4O_9 ; the second is a discontinuum term and results from lattice phase dimensional changes (which are significant and are the order of a few percent for U_4O_8 to a U_4O_9 phase change); and the third is also a discontinuum terms and results from the transport of atomic interstitials, atomic substitutionals, vacancies, and oxygen atoms to the phase change front (relative size is not know but may be significant because of the hyper-stoichiometry of oxygen ($UO_{2.4}$ in a U_4O_9 lattice)). To illustrate only the phase change

contribution to the relative velocity, assume that the elastic and P_K contributions to the velocity are negligible. A reference coordinate system (x_1, x_2, x_3) can be selected such that vector $\underline{a}$ is parallel to x_1 , $\underline{b}$ is parallel to x_2 , and $\underline{c}$ is parallel to x_3 . Also, the direction of x_2 is assumed locally perpendicular to the surface ∂R which is propagating with velocity $V_{i48} = (0, V_2, 0)$. Then, equations (4-10) and (4-11) give

$$v_i]_{49}^{48} = ((b_i e_{213} a_1 c_3)_{49} - (b_i e_{213} a_1 c_3)_{48}) P_{48}^+ V_2 \quad (4-12)$$

The $b_i(49)$ of the U_4O_9 lattice in direction x_2 is smaller than $b_i(48)$ of the U_4O_9 lattice, and because the alternating tensor e_{213} component is (-1) , the relative velocity across the front is the same sign as the propagation velocity V_{48} of ∂R . For U_4O_8 to a U_4O_9 phase transformation, this positive relative velocity is consistent with a volume decrease of forming U_4O_9 lattices from U_4O_8 lattices. From equation (4-12), information is not provided about the transverse components of a potential velocity discontinuity across ∂R . This could be evaluated based on the two other component forms of the L_{ijNM} operators. A discussion of which becomes complex since microcrack size fractures have been observed to form in the U_4O_9 phase. However, a microcrack deformation mechanism has not been included in this kinematic analysis.

The above developments addressed the phase change of U_4O_8 to U_4O_9 . Similar equations can be written for U_4O_9 oxidation to U_3O_8 . These equations are the same as above with "49" replaced by a "38" lattice structure identifier, and then "48" replaced by a "49" lattice structure identifier. In the case of U_3O_8 , there is a significant volume increase ($\sim 30\%$) in forms from U_4O_9 ; thus, the velocity discontinuity $\underline{v}]_{38}^{49}$ normal to the front is negative as the U_3O_8 lattice increases in volume behind a phase front. Because of the phase change volume increase, it is expected that a large number of microcracks would occur and that the U_3O_8 spent fuel would potentially be a high porosity waste form with low strength that may flake to micron sized particulates (powders). This is consistent with the above kinematic equations; however, as noted above, the kinematic equations do not include a microcrack dependent deformation response, and therefore are not complete. Moreover, for the particular case of spent fuel degradation, a microcrack response model is not of

special importance because experimental observations can be performed to characterize the deformation state of the U_3O_8 formed from isolated and composite (fragments) grains of U_4O_9 .

The next topic in this oxidation front analysis is potential stress discontinuity conditions. For shock fronts the stress discontinuity is derived from the momentum equation and is equal to the discontinuity in the momentum density across the propagating shock front. For a propagating oxidation phase front, a similar derivation can be performed; however, the discontinuity in the momentum density is assumed to be small and neglectable. By neglecting the momentum density, and since the effects of a possible interfacial surface energy between oxides of uranium has not been included, the stress equilibrium equation implies that the stress traction across the oxidation front must be continuous; thus,

$$\sigma_{ij} n_j]_{49}^{48} = 0 \quad \text{across a } \partial R \text{ oxidation front} \quad (4-13)$$

Note, that this does not mean that the stress is zero nor that all individual components of the stress tension are continuous across a propagating oxidation front.

The final part of an oxidation front analysis in this section is for the energetic components to the formation of U_4O_9 from U_4O_8 and U_3O_8 from U_4O_9 . The starting point is equation (3-4), and the integral representations given in equations (3-5) through (3-7). The arbitrary spatial domain $R + \partial R$ now contains a surface ∂R , across which functional discontinuities in the energy can arise. Thus, the domain R is subdivided into volume R^+ and R^- subsets by ∂R ; and in each volume subset equation (3-8) will apply. Across the propagating surface ∂R with velocity $\underline{V}$, which divides the volume subsets, the following equation applies

$$\int_{\partial R} (\epsilon(f)(v_i - V_i) + \Delta_{PK} \epsilon(f) P_K] v_{Ki})]_{-}^{+} n_i d\mathbf{x} = \int_{\partial R} [\sigma_{ij} v_j]_{-}^{+} n_i + h_i]_{-}^{+} n_i d\mathbf{x} \quad (4-14)$$

For the case of U_4O_8 in volume R^+ and U_4O_9 in volume R^- , V_i becomes V_{i48} , and the lattice density function P_{48} is non-zero in R^+ and P_{49} is non-zero in R^- .

In order to have a functional dependence on each of the function arguments of $\epsilon(f)$ as given in equation (3-1), the functional expansion of equation (3-3) is extended to include contributions from the entropy function η and the continuum strain tensor γ_{ij} ;

$$\begin{aligned}\epsilon(f) \equiv & \epsilon_0 + \Delta\eta\epsilon(\eta - \eta_0) \\ & + \Delta\gamma_{ij}\epsilon(\gamma_{ij} - \gamma_{ij}|_0) + \Delta P_{NM}\epsilon P_{NM} \\ & + \Delta P_K\epsilon P_K\end{aligned}\quad (4-15)$$

where the lattice reference energy state is evaluated in terms of an arbitrary internal energy ϵ_0 , arbitrary entropy η_0 , and strain state $\gamma_{ij}|_0$. Substituting equation (4-15) into (4-14) and rearranging terms, the following pointwise condition across ∂R can be obtained.

$$\begin{aligned}& (\epsilon_0 + \Delta\eta\epsilon(\eta - \eta_0))(v_i - V_{i48})]_{49}^{48} n_i \\ & = (\sigma_{ij}v_i)]_{49}^{48} n_j + h_k]_{49}^{48} n_k \\ & - (\Delta\gamma_{ij}\epsilon(\gamma_{ij} - \gamma_{ij}|_0)(v_k - V_{k48}))]_{49}^{48} n_k \\ & - (\Delta P_{NM}\epsilon P_{NM})(v_k - V_{k48}))]_{49}^{48} n_k \\ & - (\Delta P_K\epsilon P_K)(v_k + v_{Kk} - V_{k48}))]_{49}^{48} n_k\end{aligned}\quad (4-16)$$

where terms such as ϵ_0^+ , ϵ_0^- , η_0^+ , η_0^- , $\gamma_{ij}|_0^+$, and $\gamma_{ij}|_0^-$ are arbitrary reference state functions for the two lattice structures of P_{48} and P_{49} adjacent to surface ∂R . In order to simplify and eliminate several terms from equation (4-16) the previous assumption is applied that the velocity v_i^+ on the R^+ side of ∂R is zero, and the reference state functions are evaluated such that

$$\begin{aligned}\epsilon_0^+ &= 0 \\ \eta_0^+ &= \eta^+ \\ \gamma_{ij}^+|_0 &= \gamma_{ij}^+ \\ \epsilon_0^- &= \Delta\eta\epsilon^-(\eta_0^- - \eta^+) \\ \gamma_{ij}^-|_0 &= 0\end{aligned}\quad (4-17)$$

Then, equation (4-16) can be written as

$$\begin{aligned}& (\Delta\eta\epsilon^-(\eta^- - \eta^+)(v_i)_-^+ + V_{i48})n_i - h_i]_{49}^{48} n_i \\ & = \sigma_{ij}^-(v_i)_-^+ + v_i]_-^+ n_i \\ & - \Delta\gamma_{ij}\epsilon^- \gamma_{ij}^-(v_k)_-^+ + V_{k48})n_k \\ & + (\Delta P_{48}\epsilon^+ P_{48}^+ V_{i48} \\ & - \Delta P_{49}\epsilon^- P_{49}^- (-v_i)_-^+ - V_{i48})n_i \\ & - (\Delta P_K\epsilon^+ P_K^+)(v_{Ki}^+ - V_{i48}) \\ & - \Delta P_K\epsilon^- P_K^- (-v_i)_-^+ + v_{Ki}^- - V_{i48})n_i\end{aligned}\quad (4-18)$$

The continuum stress work term can be eliminated by assuming that the oxidation continuum strain rate processes occur at thermodynamic equilibrium (see equation 3-11), which implies that

$$\sigma_{ij}^- = \Delta\gamma_{ij}\epsilon^- \quad (4-19)$$

In addition to equation (4-19), an expression developed for the continuum strain tensor across a propagating shock front^[5] can be used (which is also true across a propagating oxidation front), namely;

$$\gamma_{ij}^- = 1/2(v_i)_-^+ n_j + v_j]_-^+ n_i / (v_k)_-^+ + V_{k48})n_k \quad (4-20)$$

to show that

$$\sigma_{ij}^-(v_i)_-^+ n_j = \Delta\gamma_{ij}\epsilon^- \gamma_{ij}^-(v_k)_-^+ + V_{k48})n_k \quad (4-21)$$

Equation (4-18) can be further simplified by substituting results from equation (4-4) to replace expressions containing P_{49} , and from (4-10) to replace the discontinuum relative velocity $v_i]_-^+$ term in the remaining part of the stress work expression. With these substitutions, equation (4-18) can be written as

$$\begin{aligned}& (\Delta\eta\epsilon^-(\eta^- - \eta^+)(v_i)_-^+ + V_{i48})n_i - h_i]_{49}^{48} n_i = \\ & - (\Delta P_{48}\epsilon^+ - \Delta P_{49}\epsilon^-)P_{48}^+ V_{i48}n_i \\ & - \sigma_{ik}^-(L_{ijNM}]_{48}^{49} P_{48}^+ V_{j48}n_k \\ & - (\Delta P_K\epsilon^+ - \Delta P_K\epsilon^-)P_K^+ V_{i48}n_i\end{aligned}$$

$$\begin{aligned}
& - \sigma_{ij}^-(L_{ikk})_{48}^{49} P_K^+] v_{k48} n_j \\
& - (\Delta P_K \epsilon P_K] v_{Ki})_{48}^{49} n_i \\
& - \sigma_{ik}^-(L_{ijk} P_K] v_{Kj})_{48}^{49} n_k \\
& - \Delta P_K \epsilon \dot{p}_K] n_j]_{48}^{49} n_j \quad (4-22)
\end{aligned}$$

The phase change energy condition of equation (4-16) can be written in forms different from that in equation (4-22). This form of equation (4-22) expresses the net dissipation entropy discontinuity $\Delta \eta \epsilon - \eta^*$ across a propagating phase change front, which is the total entropy energy change minus the net heat flux across the front. For thermodynamic processes, this dissipation entropy change is always non-negative. The terms on the right hand side of equation (4-22) provide the chemical potential energy changes from the oxidation phase transformation at the front, the work performed during the phase transformation at the front, and the net chemical potential energy transported by lattice atoms and vacancies to the front. A separation of energy terms across a front such that the thermodynamic energy of the oxidation reaction for the UO_2 transformation to U_4O_9 is not as readily discerned from equation (4-22) as it was for the homogeneous oxidation case described in equations (3-13) and (3-14). To write such a separation, the rate of change for the singular surface terms $\dot{p}_K]$ of oxygen, interstitial, substitutional, and vacancies concentrations must be expressed in terms of the lattice transformation rate $P_{48}^+]$ $V_{i48} n_i$. In the case of oxygen, one oxygen atom is removed at the front for each lattice cell of $P_{48}]$ transformed to a $P_{49}]$ cell; thus,

$$\dot{p}_O] n_i] n_i = + P_{48}^+] V_{i48} n_i \quad (4-23a)$$

$$\dot{p}_O] n_i] n_i = - P_{49}^+] (v_i)_-^+ + V_{i48}) n_i \quad (4-23b)$$

However, equation (4-22) combines the chemical potential energy of oxygen on the plus and minus sides of the front. Thus, to simplify equation (4-22), a mechanistic assumption for the oxygen source will be made; namely, the oxygen supplied for the oxidation reaction is provided from the excess oxygen on the U_4O_9 (minus) sides of the front. In addition to this assumption, it will be assumed that the interstitial, substitutional, and

vacancy concentrations across the oxidation front are conserved; thus

$$\dot{p}_I] n_i = \dot{p}_S] n_i = \dot{p}_V] n_i = 0 \quad (4-23c)$$

Using the results of equation (2-23), and the above discussion of net dissipation entropy energy, equation (4-22) can be written as

$$\begin{aligned}
& \Delta \eta \epsilon - \eta^* (v_i)_-^+ + V_{i48}) n_i = \quad (4-24) \\
& + ((\Delta P_{48} \epsilon^+ + \Delta P_O \epsilon^- - \Delta P_{49} \epsilon^-) \delta_{kj} \\
& + \sigma_{ij}^- L_{ikNM}]_{48}^{49} - \sigma_{ij}^- L_{ikO} (q_{49})) P_{48}^+] v_{k48} n_j \\
& - ((\Delta P_K \epsilon^+ + \Delta P_K \epsilon^-) \delta_{kj} + \sigma_{ij}^- L_{ikk}]_{48}^{49}) \\
& \quad \times (P_K^+] + P_K^-]) v_{k48} n_j \\
& - (\Delta P_K \epsilon \delta_{kj} - \sigma_{ij}^- L_{ikk})_{48}^{49} \\
& \quad \times (P_K^+] v_{Kk}^+ + P_K^-] v_{Kk}^-) n_j
\end{aligned}$$

Equation (4-24) provides the thermodynamic rates and nonequilibrium thermodynamic forces terms for oxidation across a propagating phase transformation front. This equation is an analog to equation (3-14) for the spatially homogeneous phase transformation of UO_2 to U_4O_9 . The positive and negative signs for the thermodynamic forces are the same because the rate $P_{48}^+]$ $V_{i48} n_i$ is positive since it is written with normal n_i ($n_i = n_i^- = -n_i^+$ and the front velocity V_{i48} is positive into the $P_{48}^+]$ spatial domain of a UO_2 grain. The following section will use Onsager's approach to relate the thermodynamic rates and conjugate thermodynamic force terms for the case of U_4O_8 transforming to U_4O_9 . The energy change equation for the phase transformation of U_4O_9 to U_3O_8 would have the same terms as those in equation (4-24); the differences would be the initial "48" lattice is replaced by the "49" lattice, and the final "49" lattice is replaced by the "38" lattice.

Equation (4-24) extends the equilibrium thermodynamics developed for treating nonstoichiometric energy contributions.^[7,8] The equilibrium thermodynamic representations do not address the kinetics (rate) of approaching a thermodynamic equilibrium state. In terms of the above equation, the thermodynamic equilibrium

state, in terms of Gibbs,^[9] would be attained when the coefficients of the rate terms on the right hand side of equation (4-24) are zero. Thus, the oxidation front velocity and diffusion rates would be zero because the thermodynamic forces are all zero at thermodynamic equilibrium.

NONEQUILIBRIUM THERMODYNAMICS PHASE TRANSFORMATIONS

In the previous section, the dissipation energy rate in equation (4-24) is expressed in terms of a phase transformation front rate tensor $P_{48}^+ V_{i48} n_j$ and mass transport tensors $P_K V_{k48} n_j$ and $P_K v_{Kk} n_j$. The tensor nature for these three rates results from the potential for doing work in the tangential directions of the oxidation surface by deforming the surface and by mass transport on the surface. This requires at an atomic scale the evolution of tangential strains and discontinuities from the formation of lattice defects such as point species, line species, or surface species. These defects are commonly known as vacancies, dislocations, and microcracks. In the following the potential tangential motion from strains and from line and surface lattice defects will not be considered. To analyze discontinuities from the line and surface defect species would require that the relative velocity and deformation expressions introduced in equations (2-1) and (2-5) be extended to include dislocation density and microcrack density terms. The neglect of these terms results in approximations because the shear work is not included and the energetics of lattice defects production are omitted.

The terms will be neglected by using the trace of the tensor $V_{i48} n_j$; which is $V_{i48} n_i$. The other tensor rate for mass transport relative to the lattice will be included in the model for oxidation phase transformation across a front. This will make the thermodynamic model consistent with the relative velocity and deformation representation which included the contributions of lattice size changes from vacancy, interstitial, substitutional, and oxygen concentrations.

With this simplification, the thermodynamic rate terms are $P_{48}^+ V_{i48} n_i$, $(P_K^+ + P_K^-) V_{i48} n_i$, and $(P_K^+ v_{Kk}^+ + P_K^- v_{Kk}^-) n_j$. From equation (4-24), the conjugate thermodynamic forces are

$$\begin{aligned} T_{48} &\equiv \Delta P_{48} \epsilon^+ + \Delta P_O \epsilon^- - \Delta P_{49} \epsilon^- \\ &+ \sigma_{ij}^- L_{ijMN} \Big]_{48}^{49} - \sigma_{ij}^- L_{ijO}(q_{49}) \end{aligned} \quad (5-1a)$$

$$T_K \equiv \sigma_{ij}^- L_{ijK} \Big]_{48}^{49} - \Delta P_K \epsilon \Big]_{48}^{49} \quad (5-1b)$$

$$T_{Kkj} \equiv \sigma_{ij}^- L_{ikk} \Big]_{48}^{49} - \Delta P_K \epsilon \Big]_{48}^{49} \delta_{kj} \quad (5-1c)$$

where T_{48} and T_K are scalar thermodynamic forces and T_{Kkj} is a second order tensor thermodynamic force. The Onsager form of first order operator equations to couple the thermodynamic rate terms and their conjugate forces are

$$\begin{aligned} P_{48}^+ V_{i48} n_i &= \mathcal{L}_{48\ 48} T_{48} + \mathcal{L}_{48K} T_K \\ &+ \mathcal{L}_{48Kkj} T_{Kkj} \end{aligned} \quad (5-2a)$$

$$\begin{aligned} (P_K^+ + P_K^-) V_{i48} n_i &= \mathcal{L}_{K48} T_{48} + \mathcal{L}_{KK} T_K \\ &+ \mathcal{L}_{KKkj} T_{Kkj} \end{aligned} \quad (5-2b)$$

$$\begin{aligned} (P_K^+ v_{Kk}^+ + P_K^- v_{Kk}^-) n_j &= \mathcal{L}_{Kkj48} T_{48} \\ &+ \mathcal{L}_{KkjK} T_K + \mathcal{L}_{KkjKmn} T_{Kmn} \end{aligned} \quad (5-2c)$$

where the set of $\{\mathcal{L}\}$ operators are Onsager coefficients that operate on the thermodynamic forces to provide the thermodynamic rates. These coefficients are phenomenological quantities that can be determined experimentally.

For example, if experiments establish that the rate (kinetics) for the phase transformation propagation velocity of the oxidation front is diffusion controlled, then the thermodynamic force T_{Kkj} , which is the diffusion force, is the dominant one and the coefficient $\mathcal{L}_{48Kkj}$ can be established. On the other hand, if the phase change energy force T_{48} is controlling the front velocity of phase changes, then it is $\mathcal{L}_{48\ 48}$ that experiments will isolate for evaluation.

At the present time, experiments have established that nonstoichiometric oxidation phase changes are occurring in spent fuel. This probably means that fission products from fission events and actinides created from neutron capture/decay processes are stabilizing lattice structures. This suggests that a

consistent thermodynamic model which represented a dependence on different concentrations of fission products and actinides should be developed for comparisons with experimental data. The concentration of fission products and actinides are represented in an aggregated approximation by the interstitial and substitutional density functions $P_I]$ and $P_S]$, respectively. As a first approximation, these two densities should monotonically increase with the number of fission events per unit volume of reactor fuel, which is commonly termed "burnup." Thus, in a linear model, the approximate fission products and actinide concentrations are

$$\begin{aligned} P_I] &= P_I]_o + \Delta_f P_I] f \\ P_S] &= P_S]_o + \Delta_f P_S] f \end{aligned} \quad (5-3)$$

where f is the accumulated fission events (burnup) of the spent fuel, the coefficients of f can be aggregately approximated from radionuclide fission product and actinide data, and the terms with subscript "o" are initial coefficients that can be used to test possible effects of some BWR spent fuels that have several initial percent of burnable poisons such as gadolima.

The difficult part of such a model is that the influence of $P_I]$ and $P_S]$ on the thermodynamic rates can occur in either the set of Onsager coefficients $\{\mathcal{L}\}$ or the set of thermodynamic forces $\{\mathbf{T}\}$; or both sets. In any of the three possible cases, the general form of equation (5-2) permits one to derive a thermodynamically consistent model to describe burnup effects on the kinetics of oxidation phase transformation in spent fuel. In the following, the approximation given in equation (5-3) is used to represent kinetic influences of burnable poisons in spent fuel and the degree of spent fuel burnup.

For two simple illustrative oxidation response models, consider first the case where the phase front has a constant velocity of propagation into spent fuel grains; and for the second case assume the phase front velocity has a square root of time dependence. In case one, it is assumed that the energy kinetics of force $\mathbf{T}_{48}$ dominates the rate response; and for case two it is assumed that the diffusion kinetics of force $\mathbf{T}_{Kkj}$ dominates the rate response. From equations (5-2a) and (5-3), consistent thermodynamic models that have a linear burnup dependence on these thermodynamic forces are given simply by

Case 1

$$P_{48}^+ V_{i48} n_i = \mathcal{L}_{48\ 48} (\mathbf{T}_{48o} + \Delta_f \mathbf{T}_{48} f) \quad (5-4a)$$

Case 2

$$P_{48}^+ V_{i48} n_i = \mathcal{L}_{48Kkj} (\mathbf{T}_{Kkjo} + \Delta_f \mathbf{T}_{Kkj} f) \quad (5-4b)$$

In Case 1, the velocity V_{i48} has a linear dependence on burnup fissions f . In Case 2 the square root time dependence occurs as a result of the thermodynamic force (the $\Delta P_K \epsilon]$ term) decaying in time as the thickness of the oxidation zone around the perimeter of a grain increases in thickness.

These two models were idealized and presented to illustrate the utility of a general formulation that uses nonequilibrium thermodynamics for relationships. It should be clear, however, that this thermodynamic approach must be coordinated with an experimental approach. Only then can the kinetics problem of oxidation and phase transformation of radioactive spent fuel be adequately understood to address performance and degradation issues relative to repository analysis and design.

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