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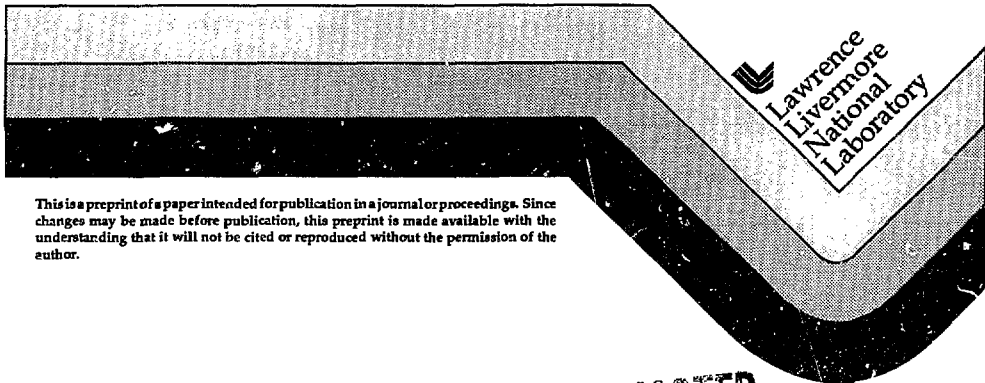
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Oxidation Phase Transitions in Spent Fuel**

**R.B. Stout  
E.J. Kansa  
A.M. Wijesinghe**

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# KINEMATICS AND THERMODYNAMICS OF NON-STOICHIOMETRIC OXIDATION PHASE TRANSITIONS IN SPENT FUEL

R. B. STOUT, E.J. KANSA, AND A.M. WIJESINGHE  
Univ. of California/LLNL, P.O. Box 808, L-2C1, Livermore, CA 94551

## ABSTRACT

At low temperatures ( $<200^{\circ}\text{C}$ ), spent fuel from power reactors oxidizes from its  $\text{UO}_2$  lattice to a  $\text{U}_4\text{O}_9$  lattice but with an oxygen-to-uranium (O/U) ratio of  $\sim 2.4$ . Also, the weight gain time response has a plateau as the O/U approaches 2.4. Part of this response results from a geometrical dependency as a  $\text{U}_4\text{O}_9$  oxidation front propagates into grain volumes of  $\text{UO}_2$ . It may also be indicative of a metastable, non-stoichiometric  $\text{U}_4\text{O}_9$  phase whose existence may inhibit the transition kinetics to the next expected phase of  $\text{U}_3\text{O}_8$ . To gain a mechanistic understanding and to plan future oxidation tests, lattice kinematic and thermodynamic models are developed for lattice deformations and energetics of lattice phase changes ( $\text{UO}_2 \rightarrow \text{U}_4\text{O}_9 \rightarrow \text{U}_3\text{O}_7 \rightarrow \text{U}_3\text{O}_8$ ) that include zeroth order influences on oxidation kinetics due to interstitial oxygen atoms and vacancies plus interstitial and substitutional actinides and fission decay products in spent fuel.

## 1. Introduction

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  $\text{UO}_2$  fuels with burnable poisons (primarily gadolinia in BWR rods), the other elements with significant atomic densities in spent fuel evolve from neutron reactions and fission plus fission decay events during reactor operation. Due to the nuclear decay processes the intrinsic isotopic composition and activity of spent fuel will continue to evolve after it is removed from reactors; and its radioactivity will decay to background levels 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 chemical responses in spent fuel and any potential degradational impacts on repository design and performance. The oxidation response of

spent fuel is one such chemical response that can impact waste package design and performance assessment. One potential impact is the dissolution response of other spent fuel oxidation phases in the event of water contact. The oxidation of spent fuel results in an initial phase change of the  $\text{UO}_2$  lattice to a  $\text{U}_4\text{O}_9$  lattice,<sup>1,2</sup> and the next phase change is probably to  $\text{U}_3\text{O}_8$  although it has not been observed yet at low temperatures ( $<200^\circ\text{C}$ ) in these experiments. The  $\text{U}_4\text{O}_9$  lattice is non-stoichiometric with an oxygen-to-uranium weight ratio (O/U) at  $\sim 2.4$ . Preliminary indications are that the  $\text{U}_4\text{O}_9$  has a O/U of  $\sim 2.4$  as it transforms from the  $\text{UO}_2$  phase.<sup>1,2</sup> Also, in the oxygen weight gain versus time response, a plateau appears as the O/U approaches  $\sim 2.4$ . Part of this plateau response is due to geometrical effects of a  $\text{U}_4\text{O}_9$  phase change front propagating into  $\text{UO}_2$  grain volumes. However, the plateau time response may be indicative of a metastable phase change delay kinetics before undergoing a phase transformation to  $\text{U}_3\text{O}_7$ , or a stabilized  $\text{U}_4\text{O}_9$  phase that has a diffusional related delay time until the oxygen density can attain a critical value to satisfy the stoichiometry and energy conditions for subsequent phase changes to  $\text{U}_3\text{O}_8$ . In this brief paper, a model to describe only spatially continuous oxidation phase change kinetics will be discussed. Additional model development activities are required to describe spatially discontinuous oxidation phase change processes across a propagating phase change front.

To describe spatial continuous oxidation phase change kinetics, lattice models for deformation and energetics are derived. The vector basis of this idealized/pseudo lattice model is not the same as that used in the physical lattice cell representations for the atomic positions in crystallography; the geometrical vector attributes of this lattice model were devised for the mathematical purpose of identifying and representing the deformation and energetic evolution of idealized chemical phases during the oxidation of  $\text{UO}_2$  spent fuel. Furthermore, this deformation and energetic formulation is different from the approaches used in continuum mechanics of solids<sup>3,4</sup> and the classical equilibrium thermodynamic analysis.<sup>5-11</sup> Here concepts from statistical mechanics, discontinuum mechanics, and non-equilibrium thermodynamics<sup>12-15</sup> will be used. Stochastic density functions are defined to describe analytically the number of lattice species for the different phases, say  $P_{12}$  for  $\text{UO}_2$ ,  $P_{49}$  for  $\text{U}_4\text{O}_9$ ,  $P_{37}$  for  $\text{U}_3\text{O}_7$ , and  $P_{38}$  for  $\text{U}_3\text{O}_8$ . Each density

function has function argument variables that are physical vector attributes of their associated lattice structure and vector rates of dimensional (deformational) changes. In addition to the deformations and energetics from the above four density functions for the different phases, deformations and energetics occur from four other stochastic density functions. These four are defined for the excess number of oxygen atoms  $P_O$  not in a uranium oxidation phase (most likely interstitial oxygen atoms but some may be chemically bonded with other substitutional or interstitial atoms), for the number of substitutional atoms  $P_S$ , for the number of non-oxygen interstitial atoms  $P_I$ , and finally for the number of vacancies  $P_V$ . The substitutional and non-oxygen interstitial density functions,  $P_S$  and  $P_I$ , respectively, are aggregate densities for the neutron capture elements (mostly actinides) and the fission product elements which include the fission event elements and their subsequent decay elements.

From these definitions for the number densities of lattices of the four phases and the number densities of other atoms in the lattices, a functional representation for the relative deformation between two atoms, say A and B, will be given in the following section. From the relative deformation, various kinematic measures of material motion, such as strain, strain rate, velocity, and velocity gradients, can be written. These kinematic measures are required to express energy and stress work terms in the thermodynamic model for phase change kinetics discussed in section three. The thermodynamic model assumes the existence of an internal energy functional from which an entropy production equation is derived. The rate expressions in this entropy production provide equilibrium (no entropy production) and non-equilibrium thermodynamic conditions for phase changes (entropy production). From this thermodynamic model, there are three conditions: one is kinematic accessibility, a second is stoichiometry (atomic mass availability), and the third is energetics. It is from these conditions that a non-equilibrium thermodynamic model for phase change kinetics can be proposed. In this short paper, all the analytical details for deriving expressions will not be provided. The intent in this model development is to arrive at kinematic and thermodynamic rate relationships that will form a framework for advocating, guiding, and interpreting spent fuel oxidation testing activities. These rate relationships, which have a

thermodynamic basis, will be combined with data from oxidation testing activities to formulate a spent fuel oxidation response model for repository design and performance assessment activities.

## 2. Statistical Lattice Kinematics to Describe Phase Change Deformations

A model describing the deformation response of a contiguous set of lattice cells is developed. The model represents a lattice cell by a set of vector attributes. These vector attributes are the variables in density functions for the number of lattice cells of a particular species per unit volume. The lattice density is a stochastic function and species-dependent integrals over the set of vector attributes provide probable values for the deformation response. To arrive at this deformation response, consider a unit cell of a lattice structure to have 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  $\partial R_0$ . To represent a stochastic motion of deformation at time  $t$ , a set of velocity vector attributes  $(\dot{\underline{a}}, \dot{\underline{b}}, \dot{\underline{c}})$  is 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 lattice phase. For shorthand purposes, the species space for the six vector attributes  $\{\underline{a}, \underline{b}, \underline{c}, \dot{\underline{a}}, \dot{\underline{b}}, \dot{\underline{c}}\}$  will be 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 four likely phases of  $UO_2$ , four different density functions are defined:  $P_{12}(\underline{x}, t, q)$  denote the number density of  $UO_2$  lattice cells such that each cell contains one uranium atom,  $P_{49}(\underline{x}, t, q)$  denotes the number density of  $U_4O_9$  lattice cells such that each cell contains four uranium atoms,  $P_{37}(\underline{x}, t, q)$  denotes the number density of  $U_3O_7$  lattice cells such that each cell contains four uranium atoms, and  $P_{38}(\underline{x}, t, q)$  denotes the number density of  $U_3O_8$  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  $P_{12}$ ,  $P_{49}$ ,  $P_{37}$ , 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  $P_{12} \equiv P_{12}| + P_{12}$ ,  $P_{49} \equiv P_{49}| + P_{49}$ ,  $P_{37} \equiv P_{37}| + P_{37}$ ,  $P_{38} \equiv P_{38}| + P_{38}$  where the single bar symbol denotes the continuum response and the single square bracket denotes the discontinuum response. This decomposition analytically represents 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 as interstitial, substitutional, vacancy, and oxygen species migrate in and out of the lattice by incremental vector attributed  $(\hat{a}, \hat{b}, \hat{c})$ ; 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 velocity relative to the local lattice cell velocity ( $K \sim I, S, V, \text{ or } O$  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, lattice structure descriptors, and discussions, 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  $R_Q$ . To start, assume that the lattice cell structure is perfect and has only  $UO_2$  lattices. Then, the probable total relative velocity  $\underline{v}\}_A^B$  of point  $B$  relative to point  $A$  at time  $t$  is

$$\begin{aligned} v_i\}_A^B &= \int_{\underline{x}_A}^{\underline{x}_B} \left( \hat{a}_i e_{j\mu\nu} b_k c_m + \hat{b}_i e_{j\mu\nu} c_k a_m + \hat{c}_i e_{j\mu\nu} a_k b_m \right) P_{12}(\underline{\xi}, t, q) \\ &+ \left( a_i e_{j\mu\nu} b_k c_m + b_i e_{j\mu\nu} c_k a_m + c_i e_{j\mu\nu} a_k b_m \right) \dot{\bar{P}}_{12}(\underline{\xi}, t, q) dq d\xi_j \end{aligned} \quad (2-1)$$

which is the contribution to velocity from all lattice species (integration over  $Q$ ) of volume elements (example,  $d\xi_j e_{j\mu\nu} b_k c_m$ ) along an arbitrary path from spatial point  $\underline{x}_A$  to  $\underline{x}_B$ . For notational shorthand purposes, equation (2-1) can be written in terms of functional operators as

$$v_i\}_A^B \equiv \hat{L}_{ij12} P_{12} \Delta x_j\}_A^B + L_{ij12} \dot{\bar{P}}_{12} \Delta x_j\}_A^B \quad (2-2)$$

where the definitions for operators  $\hat{L}_{ij12}(\cdot)\Delta x_j\}_A^B$  and  $L_{ij12}(\cdot)\Delta x_j\}_A^B$  follow from equation (2-1) and the  $\Delta x_j\}_A^B$  is a shorthand for indicating spatial integration from point  $\underline{x}_A$  to point  $\underline{x}_B$ . The lattice density rate  $\dot{\bar{P}}_{12}$  will be described later when it is decomposed into continuum and discontinuum terms. 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  $(\hat{\underline{a}}, \hat{\underline{b}}, \hat{\underline{c}})$ , and is represented in the relative velocity with operator

$$L_{ijK}(\cdot) \equiv \int_Q \left( \hat{a}_i e_{j\mu\nu} b_k c_m + \hat{b}_i e_{j\mu\nu} c_k a_m + \hat{c}_i e_{j\mu\nu} a_k b_m \right)_K (\cdot) dq \quad (2-3)$$

Then, the relative velocity of equation (2-2) in a  $UO_2$  spent fuel lattice with the added dependence on oxygen, interstitial, substitutional, and vacancy densities becomes

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

$$v_i\}_A^B = \left( \hat{L}_{ij12} P_{12} + L_{ij12} \dot{\bar{P}}_{12} \right) \Delta x_j\}_A^B \quad (2-4b)$$



$$v_i\}_A^B = \left( L_{ij12} \dot{\bar{P}}_{12} \right) + L_{ijk} \dot{\bar{P}}_{\kappa} \left) \Delta x_j\}_A^B \quad (2-4c)$$

where K has four letter indices O, I, S, and V to obtain relative velocity contributions from oxygen, interstitial, substitutional, and vacancy density changes and continuum and discontinuum relative velocities  $v_i\}_A^B$  and  $v_i\}_A^B$  are defined in terms of the lattice cell decomposition functions  $P_{12}\}_A^B$  and  $P_{12}\}_A^B$ .

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

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

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

From equation (2-4), a 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. Then, the total relative deformation of point B relative to point A, denoted by  $\chi\}_A^B$  is at time  $t = \Delta\tau$ , for any arbitrary lattice cell species densities  $P_{MN}$ , given by

$$\begin{aligned} \chi_i\}_A^B &= X_i\}_A^B + \int_0^{\Delta\tau} v_i\}_A^B dt \\ &= X_i\}_A^B + \left( \dot{L}_{ijMN} P_{MN} \right) + \dot{L}_{ijMN} \dot{\bar{P}}_{MN} + \left( L_{ijk} \dot{\bar{P}}_{\kappa} \right) \Delta x_j\}_A^B \Delta\tau \end{aligned} \quad (2-5a)$$

where the functional operators  $L_{ijMN}(\ )\Delta x_j\}_A^B \Delta\tau$  and  $L_{ijk}(\ )\Delta x_j\}_A^B \Delta\tau$  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  $P_{MN}\}_A^B$  and  $P_{MN}\}_A^B$ . 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 [14-15] for analog derivations)

$$\gamma_{ij}\}_A^B = \left( \dot{L}_{ijMN} + \dot{L}_{jiMN} \right) P_{MN}\}_A^B \Delta\tau + \left( L_{ijMN} + L_{jiMN} \right) \dot{\bar{P}}_{MN}\}_A^B \Delta\tau + \text{second order terms} \quad (2-6)$$

For the present analysis, only the linear terms of  $P_{MN}$  and  $\dot{P}_{MN}$  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 the kinematic measures of deformation that will be used in the following section on thermodynamic modelling.

### 3. Statistical Lattice Energetics and Phase Transformation Thermodynamics

A nonequilibrium thermodynamic model is developed for the rate of entropy production during oxidation phase transformations of spent fuel. The model represents 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, an oxidation response functional can be written that expresses the kinetics of phase changes dependent on the thermodynamic force for transport and the thermodynamic force for phase change energetics. This representation is for a spatially continuous phase change process; additional analysis is necessary to extend the thermodynamic expressions obtained here to the case of a phase change front that propagates as a spatial surface of discontinuity between two phases.

To begin, 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 four lattice phase density functions  $P_{12}(\underline{x}, t, q)$ ,  $P_{49}(\underline{x}, t, q)$ ,  $P_{37}(\underline{x}, t, q)$ ,  $P_{38}(\underline{x}, t, q)$ , and the four density functions for atom and vacancy concentrations,  $P_0(\underline{x}, t, q)$ ,  $P_I(\underline{x}, t, q)$ ,  $P_S(\underline{x}, t, q)$ ,  $P_V(\underline{x}, t, q)$ ; thus,

$$\bar{\epsilon}(\underline{x}, t) = \epsilon(\eta, \underline{\gamma}, P_{12}, P_{49}, P_{37}, P_{38}, P_0, P_I, P_S, P_V) \equiv \epsilon(f) \quad (3-1)$$

where  $f$  is shorthand to replace the writing of the ten 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  $t$  greater than an initial time at  $t=0$ . In addition to existence of  $\epsilon$ , 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  $\epsilon$  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  $P_{12}$ ,  $P_{49}$ ,  $P_{37}$ , and  $P_{38}$ , with their associated energies, and into which oxygen atoms, interstitial atoms, substitutional atoms, and vacancies defect densities of  $P_0$ ,  $P_I$ ,  $P_S$ ,  $P_V$ , respectively, are inserted with their associated energies. This can be written as

$$\bar{\epsilon}(\underline{x}, t) = \epsilon(f) \equiv \Delta P_{12} \epsilon(f) P_{12}] + \Delta P_{49} \epsilon(f) P_{49}] + \Delta P_{37} \epsilon(f) P_{37}] + \Delta P_{38} \epsilon(f) P_{38}] \\ + \Delta P_0 \epsilon(f) P_0] + \Delta P_I \epsilon(f) P_I] + \Delta P_S \epsilon(f) P_S] + \Delta P_V \epsilon(f) P_V] \quad (3-2)$$

where the  $\Delta_{( )}$   $\epsilon$  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), 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 subset  $R + \partial R$  in  $R_0 + \partial R_0$ ,

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

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

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

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

$$\dot{\bar{W}} = \int_R \dot{f}_j v_j d\mathbf{x} + \int_{\partial R} \dot{\sigma}_{ij} n_j v_i d\mathbf{x} \quad (3-6)$$

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

$$\dot{\bar{E}} = \int_R \dot{\partial}_t \epsilon(f) d\mathbf{x} + \int_{\partial R} \epsilon(f) v_i n_i + \Delta P_K \epsilon(f) P_K v_{K_i} n_i d\mathbf{x} \quad (3-7)$$

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  $\partial R$  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 ( $v_{K_i} n_i$ ) with respect to the lattice velocity  $v_i$ . The surface integral expression in equations (3-5), (3-6), and (3-7) over  $\partial R$  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  $R$ :

$$\int_R (\Delta_n \epsilon \dot{\eta} - \dot{H}_o - \partial_i \dot{h}_i) d\mathbf{x} = \int_R \left( (\dot{f}_j + \partial_j \dot{\sigma}_{ij}) \cdot v_j + \epsilon_{ij} \partial_i v_j - \Delta_{T_{K_i}} \epsilon \dot{\gamma}_{ij} \right) d\mathbf{x} \quad (3-8)$$

$$- \Delta P_{NM} \dot{\epsilon} \dot{\bar{P}}_{NM} \} - \Delta P_K \dot{\epsilon} \dot{\bar{P}}_K \} - \partial_i (\Delta P_K \epsilon) P_K \} v_{Ki} \}$$

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  $\Delta \eta \dot{\epsilon} \dot{\eta}^*$ . 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

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

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,  $\dot{\eta}^*$ , 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

$$\int_R \Delta \eta \dot{\epsilon} \dot{\eta}^* d\underline{x} = \int_R \left( \left( \sigma_{ij} - \Delta \gamma_{ij} \epsilon \right) \dot{\gamma}_{ij} \right) + \sigma_{ij} L_{ijMN} \dot{\bar{P}}_{MN} \quad (3-10)$$

$$+ \sigma_{ij} L_{ijK} \dot{\bar{P}}_K \} - \Delta P_{NM} \dot{\epsilon} \dot{\bar{P}}_{NM} \} - \Delta P_K \dot{\epsilon} \dot{\bar{P}}_K \} - \partial_i (\Delta P_K \epsilon) P_K \} v_{Ki} \} d\underline{x}$$

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  $\dot{\bar{P}}_{MN}$ , atom/vacancy density rate change process  $\dot{\bar{P}}_K$ , and atom/vacancy density flux processes  $\dot{\bar{P}}_K \} v_{Ki}$ . In this analysis, all strain rate processes are assumed to occur at thermodynamic equilibrium, hence

$$\sigma_{ij} = \Delta \gamma_{ij} \epsilon \quad (3-11)$$

and this eliminates the strain rate term in equation (3-10). More importantly, this assumption also means, for modeling purposes here, that all 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  $UO_2$  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  $UO_2$  to  $U_4O_9$  to  $U_3O_7$  to  $U_3O_8$  for a volume of spent fuel in an arbitrary spatial domain  $R$ . To transform from  $UO_2$  to only  $U_4O_9$ , the lattice rates  $\dot{\bar{P}}_{12}$  and  $\dot{\bar{P}}_{49}$  are the only non-zero lattice rates. In addition, the interstitial oxygen atomic density in the idealized lattice of  $UO_2$  has a discontinuous transition in density as the  $U_4O_9$  lattice phase is formed during the transformation from  $UO_2$  to  $U_4O_9$ . As per the discussion of cubic volumes in section 2, each cubic volume of a created  $U_4O_9$  lattice, with its four uranium atoms of the  $P_{49}$  lattice, will remove four  $UO_2$  cubic lattice volumes, each of which would contain one uranium atom, and in addition one oxygen interstitial from the  $P_O$  oxygen density would be removed to 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  $P_{12}$  and  $P_{49}$ , and the oxygen density function  $P_O$  relative to the two different lattices as

$$\dot{\bar{P}}_{49} \Leftrightarrow -4\dot{\bar{P}}_{12}; \dot{\bar{P}}_{49} \Leftrightarrow -\dot{\bar{P}}_{O12} - \dot{\bar{P}}_{O49} \quad (3-13a \ \& \ b)$$

where (3-13a) functionally expresses a removal rate of four  $UO_2$  lattices at the rate one  $U_4O_9$  lattice is formed and (3-13b) functionally expresses the  $\dot{\bar{P}}_{O12}$  removal rate of all oxygen from the  $UO_2$  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  $UO_2$  lattice transforms to a  $U_4O_9$  lattice, i.e.,

$$\dot{\bar{P}}_{1149} \Leftrightarrow -\dot{\bar{P}}_{1122}; \dot{\bar{P}}_{S149} \Leftrightarrow -\dot{\bar{P}}_{S122}; \dot{\bar{P}}_{V149} \Leftrightarrow -\dot{\bar{P}}_{V122} \quad (3-13c)$$

Substituting equation (3-11) and expressions (3-13) into equation (3-10), and considering only the  $UO_2$  to  $U_4O_9$  transformation, the dissipation entropy energy rate can be written as

$$\int_R \Delta \eta \epsilon \dot{\eta}^* \Big|_{12}^{49} d\bar{x} = \int_R \left[ \left( \sigma_{ij} L_{ij} \Big|_{12}^{49} - \sigma_{ij} L_{ij0} \Big|_{12}^{49} + 4\Delta P_{12} \epsilon + \Delta P_0 \epsilon - \Delta P_4 \epsilon \right) \dot{\bar{P}}_{49} \right] \quad (3-14)$$

$$+ \left( \sigma_{ij} L_{ij0} \Big|_{12}^{49} - \Delta P_0 \epsilon \Big|_{12}^{49} \right) \dot{\bar{P}}_{O149} + \left( \sigma_{ij} L_{ij} \Big|_{12}^{49} - \Delta P_1 \epsilon \Big|_{12}^{49} \right) \dot{\bar{P}}_{1149}$$

$$+ \left( \sigma_{ij} L_{ijS} \Big|_{12}^{49} - \Delta P_S \epsilon \Big|_{12}^{49} \right) \dot{\bar{P}}_{S149} + \left( \sigma_{ij} L_{ijV} \Big|_{12}^{49} - \Delta P_V \epsilon \Big|_{12}^{49} \right) \dot{\bar{P}}_{V149} - \partial_i (\Delta P_K \epsilon) P_K \Big|_{V_{K1}} v_{K1} d\bar{x}$$

where terms such as  $\sigma_{ij} L_{ij} \Big|_{12}^{49}$  operating on  $\dot{\bar{P}}_{49}$  is shorthand notation for the stress work during the  $UO_2$  to  $U_4O_9$  transformation,  $(\sigma_{ij} L_{ij49} - 4\sigma_{ij} L_{ij12}) \dot{\bar{P}}_{49}$  (the second term results from expression (3-13a), and terms such as  $\Delta P_S \epsilon \Big|_{12}^{49}$  operating on  $\dot{\bar{P}}_{S149}$  denote the internal energy changes for substitutional atoms in the  $U_4O_9$  lattice relative to the  $UO_2$  lattice,  $(\Delta P_S \epsilon_{49} \dot{\bar{P}}_{S149} - \Delta P_S \epsilon_{12} \dot{\bar{P}}_{S149})$  (the second term results from expression (3-13c)). From equation (3-14), the dissipation entropy rate for  $UO_2$  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  $UO_2$ , i.e., no fission products ( $P_S = P_1 = 0$ ) and stoichiometric phase transformations, then only the rate  $\dot{\bar{P}}_{49}$  and the flux  $P_{O1} v_{O1}$  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  $UO_2$  spent fuel transforms to a  $U_4O_9$  lattice with non-zero values for  $P_S$  and  $P_1$  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<sub>4</sub>O<sub>9</sub> phase is a metastable energy phase relative to U<sub>3</sub>O<sub>7</sub>. Equation (3-14) could be readily modified to represent the entropy rate for a U<sub>4</sub>O<sub>9</sub> to U<sub>3</sub>O<sub>7</sub> phase transformation by replacing the previous "12" by "49" and with 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<sub>3</sub>O<sub>8</sub>, which will require additional oxygen to be transported into the U<sub>4</sub>O<sub>9</sub> lattice for the transformation to occur. At the present time, there is uncertainty about the path to U<sub>3</sub>O<sub>8</sub>; i.e., does U<sub>3</sub>O<sub>8</sub> form with the addition of sufficient oxygen directly from the nonstoichiometric U<sub>4</sub>O<sub>9</sub> lattice, or is there an intermediate temporary phase; perhaps U<sub>3</sub>O<sub>7</sub> and then to U<sub>3</sub>O<sub>8</sub>. Because U<sub>3</sub>O<sub>7</sub> is a stoichiometric accessible phase from the U<sub>4</sub>O<sub>9</sub> 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<sub>4</sub>O<sub>9</sub> lattice to the U<sub>3</sub>O<sub>8</sub> lattice. This is done by changing in equation (3-14) the existing "12" to "49" and the previous "49" to "38"; and then changing the numerical coefficients to satisfy lattice-mass balance according to the following functional expressions:

$$\begin{aligned} \dot{\bar{P}}_{38} &\Leftrightarrow -\dot{\bar{P}}_{49}; & \dot{\bar{P}}_{38} &\Leftrightarrow -\dot{\bar{P}}_{O49} - \dot{\bar{P}}_{O38} \\ \dot{\bar{P}}_{138} &\Leftrightarrow -\dot{\bar{P}}_{149}; & \dot{\bar{P}}_{S38} &\Leftrightarrow -\dot{\bar{P}}_{S49}; & \dot{\bar{P}}_{V38} &\Leftrightarrow -\dot{\bar{P}}_{V49} \end{aligned} \quad (3-15)$$

Then the thermodynamics for the entropy energy rate of U<sub>4</sub>O<sub>9</sub> to U<sub>3</sub>O<sub>8</sub> transformations is:

$$\begin{aligned} \int_R \Delta \eta \epsilon \dot{\eta}^* \Big|_{49}^{38} d\underline{x} &= \int_R \left( \left( \sigma_{ij} L_{ij} \Big|_{49}^{38} - \sigma_{ij} L_{ij0} \Big|_{49}^{38} + \Delta P_{49} \epsilon + \Delta P_0 \epsilon - \Delta P_{38} \epsilon \right) \dot{\bar{P}}_{38} \right) \\ &+ \left( \sigma_{ij} L_{ij0} \Big|_{49}^{38} - \Delta P_0 \epsilon \Big|_{49}^{38} \right) \dot{\bar{P}}_{O38} + \left( \sigma_{ij} L_{ijl} \Big|_{49}^{38} - \Delta P_l \epsilon \Big|_{49}^{38} \right) \dot{\bar{P}}_{l38} \\ &+ \left( \sigma_{ij} L_{ijs} \Big|_{49}^{38} - \Delta P_s \epsilon \Big|_{49}^{38} \right) \dot{\bar{P}}_{S38} + \left( \sigma_{ij} L_{ijv} \Big|_{49}^{38} - \Delta P_v \epsilon \Big|_{49}^{38} \right) \dot{\bar{P}}_{V38} - \partial_i (\Delta P_K \epsilon) P_K \Big|_{V_{Ki}} d\underline{x} \end{aligned} \quad (3-16)$$

The full nonequilibrium thermodynamic rate response model from equation (3-16) functionally couples the nine rate flux functions ( $\dot{\bar{P}}_{38}$ ,  $\dot{\bar{P}}_{O38}$ ,  $\dot{\bar{P}}_{l38}$ ,  $\dot{\bar{P}}_{S38}$ ,  $\dot{\bar{P}}_{V38}$ ,  $P_{O|V_{Oi}}$ ,  $P_{l|V_{li}}$ ,  $P_{S|V_{Si}}$ ,  $P_{V|V_{Vi}}$ ) 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). While such a model is analytically and thermodynamically consistent, a more restrictive and simplistic model that is still useful for experimental planning can be postulated and then subjected to experimental testing. Such a model is based on the following assumptions:

- A1. The transport (diffusion flux) of interstitial and substitutional densities  $P_I$  and  $P_S$  are negligible at the low temperature relevant to a repository (<300°C).
- A2. The transport flux of vacancies  $P_V|v_{vi}$  is not rate-limiting and can be neglected in an oxidation rate response model.
- A3. The work energy and chemical potential energy rates of taking interstitial, substitutional and vacancy densities  $P_I$ ,  $P_S$ , and  $P_V$  from the  $U_4O_9$  lattice into the  $U_3O_8$  during the phase transformations are not rate-limiting. (Remark: this does not necessarily imply that the energy increments and non-equilibria thermodynamic measures are small.)

With the above assumptions, the 21 non-equilibrium thermodynamic rate functions are reduced to  $(\dot{P}_{38}, \dot{P}_O, P_O|v_{oi})$ , which can be functionally coupled to their conjugate thermodynamic "force" measures by the following set of equations:

$$\dot{P}_{38} = \mathcal{L}_{38\ 38} T_{38} + \mathcal{L}_{38\ O} T_O + \mathcal{L}_{38\ O v_j} T_{O v_j} \quad (3-17)$$

$$\dot{P}_O = \mathcal{L}_{O\ 38} T_{38} + \mathcal{L}_{O\ O} T_O + \mathcal{L}_{O\ O v_j} T_{O v_j}$$

$$P_O|v_i = \mathcal{L}_{v_i\ 38} T_{38} + \mathcal{L}_{v_i\ O} T_O + \mathcal{L}_{v_i\ v_j} T_{O v_j}$$

where the " $\mathcal{L}$ " are a set of Onsager coefficient operators that can include the empirically observed Arrhenius activation energy term and operate on the non-equilibrium thermodynamic forces  $T$  measures defined as

$$T_{38} \equiv \sigma_{ij} I_{ij} \Big|_{49}^{38} - \sigma_{ij} L_{ijO} \Big|_{49}^{38} + \Delta P_{49} \epsilon + \Delta P_O \epsilon - \Delta P_{38} \epsilon \quad (3-18a)$$

$$T_O \equiv \sigma_{ij} L_{ijO} \Big|_{49}^{38} - \Delta P_O \epsilon \Big|_{49}^{38} \quad (3-18b)$$

$$T_{O v_i} \equiv -\partial_i (\Delta P_O \epsilon) \quad (3-18c)$$

Note that if the  $U_3O_8$  phase transformation is stoichiometric in oxygen (O/U of  $\sim 2.66$ ), then the  $\dot{P}_o]_{38}$  rate is removed from equation (3-17). In that case, the rate of oxidation response from  $U_4O_9$  to  $U_3O_8$  depends on two rate functions: the phase transformation rate  $\dot{P}_{38}]$ , and the rate of oxygen flux  $P_o]v_{oi}$ . The phase transformation rate  $\dot{P}_{38}]$  requires the phase constraints of kinematic accessibility, oxygen mass availability, and phase change energy decrease (final (38) phase energy minus initial (49) energy minus net (final to initial) lattice stress work) to be satisfied. These two rates are thermodynamically and analytically independent functions. Thus, experimental techniques can be applied wherein temperature and the atmospheric oxygen pressure are controlled independently; then a series of test measurements can be made of oxidation rate response to differentiate the phase change rate versus the diffusion rate response characteristics of spent fuel being oxidized from  $U_4O_9$  to  $U_3O_8$ . In performing these experiments over a variety of different spent fuels with different reactor burnups, the influence of the fission product concentrations in the interstitial and substitutional density functions  $P_I$  and  $P_S$  can be assessed. Also, this influence, if experimentally significant, can be represented in this model by a functional (Taylor-like) expansion of chemical potential energies  $\Delta_{P_{12}} \epsilon$ ,  $\Delta_{P_{49}} \epsilon$ ,  $\Delta_{P_{37}} \epsilon$ , and  $\Delta_{P_{38}} \epsilon$  (i.e., linear and higher order terms in  $P_I$  and  $P_S$  appear as  $\Delta_{P_{MN}} \epsilon$  is expanded to  $\Delta_{P_{M0}} \epsilon_o + \Delta_{P_K} (\Delta_{P_{MN}} \epsilon) P_K + \dots$ ). This expression would analytically introduce into an oxidation response model of equation (3-17) an explicit and thermodynamically consistent dependence on the spent fuel burnup characteristics. Finally, this thermodynamic modelling approach introduces a large number of energetic terms, and it is only with experimental activities that the sufficiency of the assumptions A1 through A3 can be evaluated.

#### 4. Summary

The oxidation of spent fuel at low temperatures has potential impacts on waste package design and performance assessment analysis of a geological repository. A preliminary model based on lattice kinematics and nonequilibrium thermodynamics is developed for homogeneous phase transformations. The kinematic model represents discontinuous lattice deformations from

fission product elements and phase changes. The thermodynamic model represents the energetics of non-stoichiometric phase transformations, the energetics of fission product elements transported from an initial lattice phase to the next lattice phase during the phase transformation, and energetics of mass transport. A simplistic model was proposed based on several assumptions. This model is useful for planning, proposing, and analyzing experiments. Additional model development is required to address the non-homogeneous phase transformation that are experimentally observed as oxidation phase change fronts propagate within grains and pellet fragments of spent fuel. The modelling problem of spent fuel oxidation can only be completed with the mechanistic knowledge and data obtained from experimental activities.

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