

CONF-960421--9

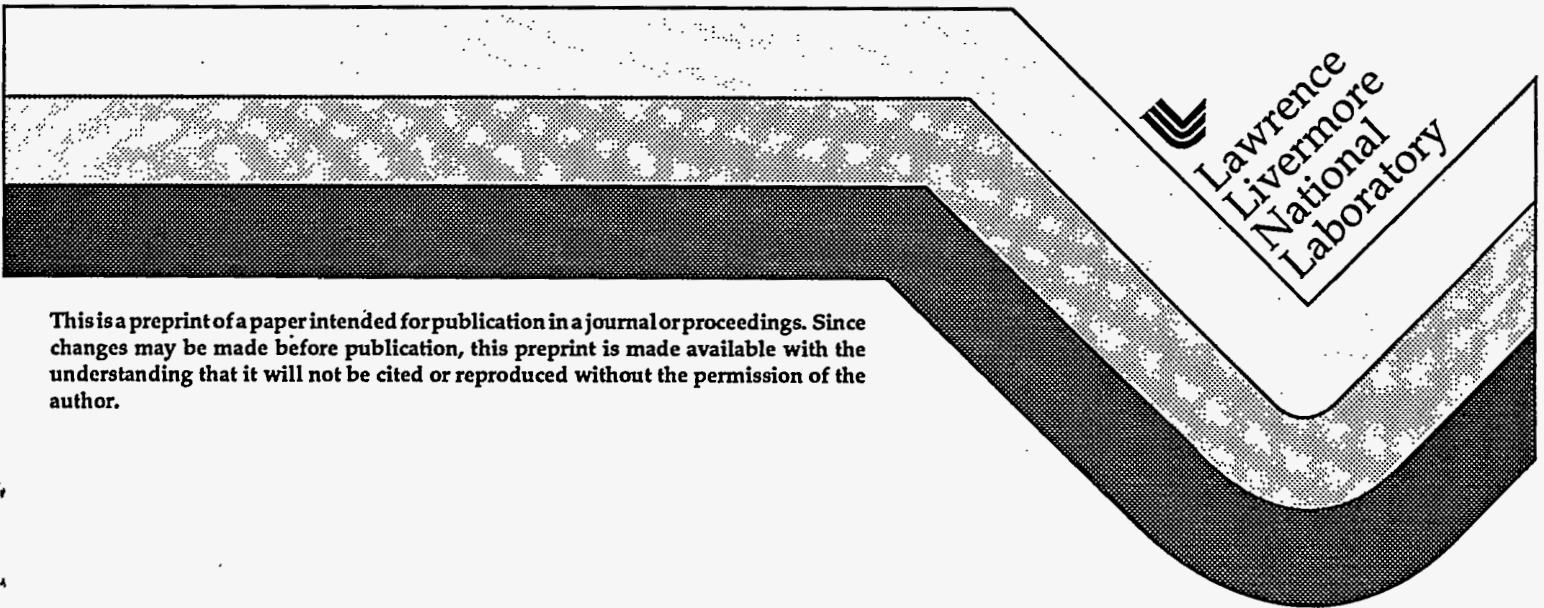
Nonequilibrium Thermodynamical Model for Spent Fuel Dissolution Rate

Ray B. Stout

RECEIVED
FEB 20 1996
OSTI

This paper was prepared for submittal to the
1996 International High Level Radioactive Waste Management Conference
Las Vegas, NV
April 29 - May 3, 1996

November 16, 1995



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Nonequilibrium Thermodynamical Model for Spent Fuel Dissolution Rate

Ray B. Stout
P.O. Box 808, L-201
Lawrence Livermore National Laboratory
Livermore, CA 94550

Introduction

A non-equilibrium thermodynamic model is developed for the dissolution response of uranium oxide spent fuels waste forms. The objective is to derive function forms for the dissolution rate that are consistent with quasi-static, irreversible thermodynamic processes. These function forms contain thermodynamic chemical potentials of both the solid (spent fuels) and the solution (water chemistries) along with a set of coefficients and parameters that can be evaluated by numerical regression of dissolution test data. Currently, detailed knowledge is not available for the atomic (mechanistic) steps and the sequence of chemical/electro-chemical reaction steps to describe the dissolution process over the range of spent fuel inventory, potential water chemistries, and temperatures. The existing approach is obtaining an experimental data base of dissolution rates for a subset of spent fuels over a range of controlled, aggressive water chemistries and temperatures. With a numerical regression algorithm, these data are used to evaluate empirical parameters in a rate law.⁹ The function form of this rate law is a product polynomial of the bulk water chemistry concentrations and temperature.¹⁰ In its present form, this function form does not have an explicit thermodynamic dependence on the uranium oxide waste form. In addition, the use of bulk concentrations in the function form for the regression analysis of the dissolution data would not explicitly account for a dependence from possible surface to bulk concentration differences due to surface adsorption and dipole layers. The following thermodynamic model uses analysis methods and physical concepts taken primarily from classical mechanics,^{4,7} colloidal foundations,⁶ thermodynamics,^{3,5,8} electro-chemistry,^{1,2} and geochemistry.¹⁰

Nonequilibrium Thermodynamic Dissolution Rate Function Forms

In the following, thermodynamic internal energy functionals are used to represent the energy responses for a generic solid and a generic liquid. The solid and liquid are in contact at an idealized wetted surface. This wetted surface is a material discontinuity, and it is also a dissolution front that propagates at an idealized dissolution velocity, \underline{V} .

The generic solid will have bulk constituents of typical UO₂ spent fuel, namely minor concentrations of other actinides, fission products, and defects in the bulk lattice structure denoted by a column matrix $\{f_s\}$. The bulk lattice is assumed to be nominally that of the UO₂ lattice structure; however, other oxide phases and adsorbed complexes as a result of solid-water chemistry reactions may exist on and in spatial neighborhoods of the wetted surface. These are denoted by a column matrix $\{f_{sL}\}$. The generic liquid will be represented with a subset of arbitrary initial/bulk constituents denoted by column matrix $\{f_L\}$. In addition the liquid has two subsets of water chemistry products formed from the dissolution of the solid and denoted by column matrices $\{f_{LS}\}$ and $\{f_{LSL}\}$. The new reaction product constituents $\{f_{sL}\}$, $\{f_{LS}\}$ and $\{f_{LSL}\}$ are interrelated to the initial solid and liquid constituents $\{f_s, f_L\}$ by stoichiometric chemical reaction expressions.

Each of the constituent densities of the solid and the liquid will be assumed to move with the particle velocity of its spatial neighborhood, \underline{v} plus its intrinsic diffusional velocity, \underline{v}_d , relative to the particle velocity. Thus the argument variables of the constituent functions f_s, f_{sL}, f_L, f_{LS} , and f_{LSL} are spatial points \underline{x} , at time, t , and species associated relative velocities, v_s, v_{sL}, v_L, v_{LS} and v_{LSL} respectively. Finally, the thermodynamic internal energy functional also has argument functions for the entropy and the elastic (recoverable) strain tensor. The entropy functions are denoted by $\eta_s(\underline{x}, t)$ and $\eta_L(\underline{x}, t)$, and the strain tensors by $\gamma_s(\underline{x}, t)$ and $\gamma_L(\underline{x}, t)$, for points \underline{x} at time t of the solid and liquid, respectively. Note that entropy and strain are material particle functions and do not have diffusional velocities relative to their material particle located at point \underline{x} with velocity $\underline{v}(\underline{x}, t)$. In the following, the effect of non-recoverable deformations with finite, discontinuous strain tensor effects will be neglected.

Using the above notation and definition of functions, the internal energy functional for the solid and liquid are defined as

$$\varepsilon_s(\eta_s, \gamma_s, \{f_s\}) \equiv \varepsilon_s(\eta_s, \gamma_s, f_s, f_{sL}) \quad \& \quad \varepsilon_L(\eta_L, \gamma_L, \{f_L\}) \equiv \varepsilon_L(\eta_L, \gamma_L, f_L, f_{LS}, f_{LSL}) \quad (1)$$

and it is assumed that a functional derivative exists with respect to each of their argument functions for all times, t , and at all points, \underline{x} , of the solid and liquid bodies $\bar{R}_s + \bar{R}_L$ plus surfaces $\partial\bar{R}_s + \partial\bar{R}_L$.

The following analysis provides some details for only the energy conditions across an arbitrary segment $\partial R]$ of $\partial\bar{R}]$ for quasi-static conditions. In equation form, the surface contribution to the energy equation can be written with some shorthand notation for arbitrary $\partial R]$ as:

$$\int_{\partial R} \left((\Delta_\eta \varepsilon \eta + \Delta_\gamma \varepsilon \gamma + \Delta_f \varepsilon f) (\underline{v} - \underline{V}) \cdot \underline{n} \right)_s^L \quad (2)$$

$$+ \Delta_f \varepsilon \{f \underline{v}\} \cdot \underline{n} \Big|_s^L - \underline{\sigma} \cdot \underline{v} \cdot \underline{n} \Big|_s^L - \underline{h} \cdot \underline{n} \Big|_s^L + \underline{J} \phi \cdot \underline{n} \Big|_s^L = 0$$

where terms for internal energy discontinuities with particle velocity, \underline{v} , minus front velocity, \underline{V} , contributions are separated from the diffusional flux velocity, \underline{v} , terms and from the energy rate terms from stress, heat flux and the quasi-static electric current/field work term. Eq. 2 can be simplified to obtain the following entropy production/dissipation equation across ∂R :

$$\int_{\partial R} \Delta_\eta \varepsilon \eta (\underline{v} - \underline{V}) \cdot \underline{n} \Big|_s^L = - \int_{\partial R} (\Delta_f \varepsilon f - e \{z f\} \phi) (\underline{v} - \underline{V}) \cdot \underline{n} \Big|_s^L \quad (3)$$

$$- \int_{\partial R} (\Delta_f \varepsilon \{f \underline{v}\} - e \{z f \underline{v}\} \phi) \cdot \underline{n} \Big|_s^L$$

In terms of the shorthand notation, the coefficients appear to be the same for both rate terms. However, when the stoichiometric equation forms for the reactions are formally incorporated, the thermodynamic force functionals describe an independent energy change for chemical reaction kinetics and an independent energy change for diffusional mass transport kinetics. Using Onsager's concepts to describe nonequilibrium or irreversible thermodynamic processes, the two rate functions are coupled by function or functional coefficients to the two thermodynamic forces of energy kinetics and diffusion mass transport kinetics. Formally these are

$$\{f\} (\underline{v} - \underline{V}) \cdot \underline{n} = L_{VV} [\Delta_f \varepsilon - e \{z\} \phi]_{energy} + L_{Vv} [\Delta_f \varepsilon - e \{z\} \phi]_{diffusion} \quad (4)$$

$$\{f \underline{v}\} \cdot \underline{n} = L_{vV} [\Delta_f \varepsilon - e \{z\} \phi]_{energy} + L_{vv} [\Delta_f \varepsilon - e \{z\} \phi]_{diffusion} \quad (5)$$

where the four coefficients L_{VV} , L_{Vv} , L_{vV} , and L_{vv} (which can be functions of $\{f\}$) couple the rate functions to the thermodynamic forces.

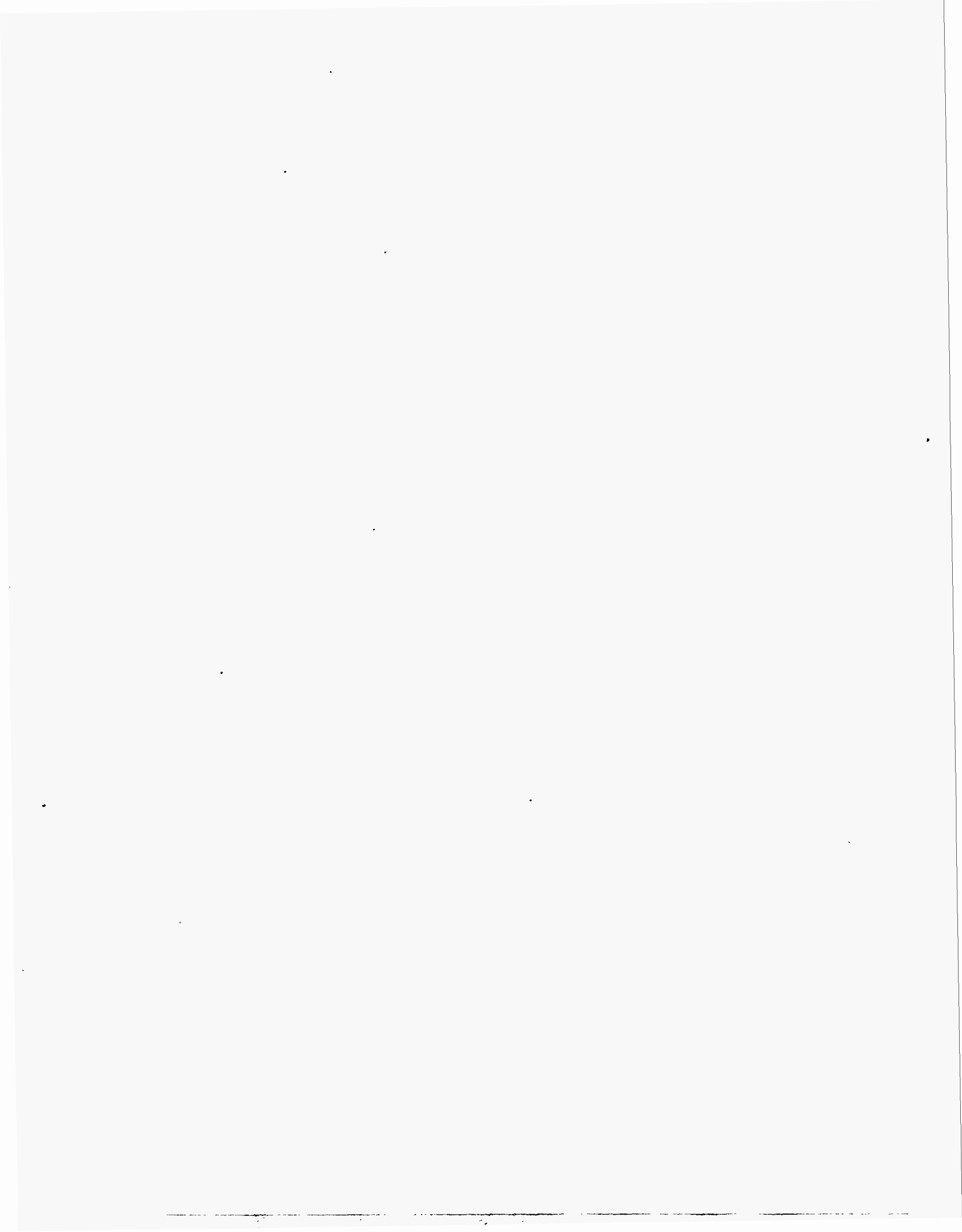
Eq. 4 provides thermodynamic function forms that should be evaluated at the dissolution front for the dissolution rate function, which is essentially the dissolution front velocity when the details of the surface particle velocities are neglected. For numerical regression analyses, particular chemical reactions with some regression parameters will be assumed; and the regression parameters evaluated based on the available thermodynamic values and dissolution data sets.

Acknowledgements

Work performed under auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract W-7506-ENG-48. The work was supported by USDOE Yucca Mountain Project and by USDOE/AECL International Agreement funding.

References

1. Antropov, L.I., *Theoretical Electrochemistry*, Mir Publishers, Moscow, 1972.
2. Bockris, J.O. and A.K. Reddy, *Modern Electrochemistry, Vols. 1 & 2*, Plenum Press, New York, 1970.
3. deGroot, S.R., and P. Mazur, *Non-equilibrium Thermodynamics*, North Holland, Amsterdam, 1962.
4. Eringen, A.C., *Mechanics of Continua*, John Wiley & Sons, New York, 1967.
5. Gibbs, J.W., *The Scientific Papers of J. Willard Gibbs, Vols. 1 & 2*, Dover Pub., New York, 1961.
6. Hunter, R.J., *Foundations of Colloid Science*, Clarendon Press, Oxford, England, 1993.
7. Jackson, J.D., *Classical Electrodynamics*, John Wiley & Sons, New York, 1962.
8. Lewis, G.N., and M. Randall, *Thermodynamics*, McGraw-Hill, New York, 1961.
9. Steward, S.A., and W.J. Gray, Comparison of uranium dissolution rates from spent fuel and uranium dioxide, Proc. 5th Annual Int'l. High-Level Rad. Waste Mgmt. Conf. (IHLRWM), Las Vegas, NV, May 22-26, 1994, 4, 2602-2608, 1994.
10. Stumm, W., and J.J. Morgan, *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, John Wiley & Sons, New York, 1981.



*Technical Information Department · Lawrence Livermore National Laboratory
University of California · Livermore, California 94551*

