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Gregory A. Henshall

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STOCHASTIC MODELING OF THE INFLUENCE OF ENVIRONMENT ON PITTING CORROSION DAMAGE OF RADIOACTIVE-WASTE CONTAINERS

Gregory A. Henshall,

Lawrence Livermore National Laboratory, P. O. Box 808, L-355, Livermore, CA 94551, USA.

ABSTRACT

A physically-based, phenomenological stochastic model for pit initiation and growth is presented as a potential tool for predicting the degradation of high-level radioactive-waste containers by aqueous pitting corrosion. Included in the model are simple phenomenological equations describing the dependence of the controlling stochastic parameters on the applied (or corrosion) potential, chloride ion concentration, and absolute temperature. Results from this model are presented that demonstrate its ability to simulate several important environmental effects on pitting.

INTRODUCTION

A multiple barrier concept currently is being employed in the development of high-level radioactive-waste (HLRW) containers for use in the potential geological repository at Yucca Mountain. One of these barriers will be constructed of a highly corrosion resistant material, such as a Ni- or Ti-base alloy. Normally, such alloys are protected by a passive oxide film, but if they become wet and Cl^- or other aggressive species are present the passive film can break down locally, causing pitting. Thus, the design of the corrosion resistant barrier must include an analysis of pitting. Modeling is a key element in this analysis because the required containment times are well beyond those for which experimental data can be collected. In particular, predictions of how changes in the container environment over these extensive time periods will affect pitting must be made.

In this paper (sponsored by the Yucca Mountain Site Characterization project), a physically-based, phenomenological stochastic model of pit initiation and growth is presented. This model is based upon the theory [1] that small fluctuations in the local conditions (*e.g.* electrolyte chemistry, fluid flow rate, surface topography, surface metallurgy) cause local breakdown of the passive surface film, resulting in the "birth" of metastable pits or "embryos". Many of these embryos become unstable when the local conditions change and repassivation, or "death", of the embryo results. Once a surviving embryo reaches a critical size or age, it becomes a permanent, or "stable," pit and cannot die. Stable pits then grow at a rate that can be computed with deterministic, *e.g.* mass transport, laws or with a stochastic model.

Several investigators have developed Monte Carlo computer codes based on this stochastic theory [2-4]. As discussed in detail elsewhere [4], these codes establish a unit area that is divided into individual "cells" to represent a metal surface in contact with an aggressive environment. Random numbers are generated and their values are compared with the

prescribed birth probability, λ , and death probability, μ , to control the initiation, growth, and death of metastable pit embryos. This Monte Carlo process is repeated during each time step for each cell, with a cell capable of containing at most one pit. If a given embryo survives for a number of time steps equal to the critical age, τ_c , then a stable pit is established in that cell. In this paper, stable pit growth also is treated stochastically because this approach was found to produce results superior to those of deterministic models [4]. Growth of a stable pit during a particular time step occurs only if a randomly generated number is less than the growth probability, γ .

One major purpose of modeling pitting corrosion of HLRW container candidate materials is to extrapolate short-time, or "accelerated", test data to the extremely long service times. Since accelerated testing will require environmental conditions more aggressive than those expected in the repository, these extrapolations will require quantitative predictions of the effects of environment on pit initiation and growth rates. Simulating the effects of environment on pitting also will be required to explore container performance for various environmental scenarios, including the expected case in which the environment changes with time.

In the context of stochastic pitting models, these goals can be achieved by describing the environmental sensitivity of the stochastic parameters: λ , μ , τ_c , and γ . Based on a limited set of experimental data, this paper presents simple, but physically reasonable, phenomenological expressions for these relationships. The purpose of this exercise was to provide the means for qualitatively illustrating the potential power of the stochastic approach for predicting the pitting response to various, probably changing, environments. Further efforts will be needed to improve the physical basis of these expressions, to expand their scope, and to fully explore their predictive capabilities.

MODEL DEVELOPMENT

Three important environmental parameters have been included in the illustrative model: applied (or corrosion) potential, E_{app} , chloride ion concentration, $[Cl^-]$, and absolute temperature, T . Other variables, such as pH, oxygen concentration and the presence of other ions in solution, will need to be included in future, more complete models.

Relating the stochastic pit initiation parameters (λ , μ , and τ_c) to E_{app} , $[Cl^-]$, and T was accomplished using the extensive experimental data of Shibata and co-workers [3,5-7], in which these relationships were explored directly. Both linear and exponential relationships between λ and E_{app} were observed in these investigations:

$$\lambda \sim \alpha (E_{app} - E_c), \quad (1a)$$

where α is a constant and E_c is the critical potential below which pit initiation cannot occur, or

$$\lambda \sim \alpha \exp(\beta E_{app}), \quad (1b)$$

where α and β are constants. The death probability was found not to be a function of E_{app} , which is consistent with its physical basis [4,8]. Further, Shibata showed [6,7] that the temperature dependencies of the pit initiation parameters can be represented by separate Arrhenius expressions. The remaining proportionalities were not given explicitly, but approximate relationships can be gleaned from the data of reference [5]:

$$\tau_c \sim \exp(-k_1 E_{app}), \quad (2)$$

$$\lambda \sim \exp(k_2 [\text{Cl}^-]), \quad (3)$$

$$\mu \sim \exp(-k_3 [\text{Cl}^-]), \quad (4)$$

$$\tau_c \sim \exp(-k_4 [\text{Cl}^-]), \quad (5)$$

where the k_i are constants.

The equation for the stable pit growth probability, γ , as a function of environment was developed from a variety of experimental data. Based on the data of Broli *et al.* [9], the current density *within a pit* increases as the temperature increases. Thus, an Arrhenius relationship between γ and T has been assumed for the present model, which may be an oversimplification. The data of Broli *et al.* also indicate that γ increases as $[\text{Cl}^-]$ increases. Further, the data of Herbsleb and Engell [10] suggest:

$$\gamma \sim [\text{Cl}^-]^a, \quad (6)$$

where a is a constant. The data of Szklarska-Smialowska and Janik-Czachor [11] show that the current density within pits increases linearly with E_{app} above a critical value. For a general pit geometry, this finding leads to [12]:

$$\gamma \sim (E_{app} - E_{crt})^b, \quad (7)$$

where E_{crt} is the critical voltage below which pits do not grow and b is a constant. For the case of hemispherical pits, $b = 0.5$.

Since the purpose of the current effort was chiefly to demonstrate the potential usefulness of including environmental effects within a stochastic model, it was simply assumed that the separate proportionalities presented above could be directly combined. No synergistic reactions between variables were considered. Therefore, combining these proportionalities and using a self-consistent scheme for denoting constants led to the following phenomenological expressions for the environmental dependence of the stochastic parameters:

$$\lambda = A_1 (E_{app} - B_1) \exp(C_1 [\text{Cl}^-]) \exp(-Q_\lambda/RT) \quad (8a)$$

or

$$\lambda = A_1 \exp(B_1 E_{app}) \exp(C_1 [\text{Cl}^-]) \exp(-Q_\lambda/RT) \quad (8b)$$

$$\mu = A_2 \exp(-C_2 [Cl^-]) \exp(-Q_\mu/RT) \quad (9)$$

$$\tau_c = A_3 \exp(-B_3 E_{app}) \exp(-C_3 [Cl^-]) \exp(+Q_\tau/RT) \quad (10)$$

$$\gamma = A_4 (E_{app} - B_4)^{B_5} ([Cl^-])^{C_4} \exp(+Q_\gamma/RT) \quad (11)$$

where the A 's, B 's and C 's are constants, the Q 's are activation energies and R is the gas constant. The expressions for λ , μ and γ allow for probabilities greater than unity (though the computer code limits their values to a maximum value of 1.0). Therefore, the units for the constants in (8)–(11) must be correctly chosen to keep these probabilities less than unity. Finally, the value of τ_c computed from (10) is truncated in the computer code to yield an integer number because time is discretized into steps.

Equations (8)–(11) were included in the Monte Carlo computer model described briefly in the introduction so that its ability to simulate the effects of environment on pit initiation and growth could be qualitatively demonstrated. To use this model for quantitative predictions of pitting, the constants in (8)–(11) would need to be evaluated from experimental data similar to those used in establishing the forms of these equations. Quantitative evaluation of these constants for a particular material was not attempted, however, because many of the required data currently are not available, and because the preliminary nature of equations (8)–(11) does not warrant such an effort. Therefore, the constants used in the following examples were simply chosen to illustrate specific capabilities of the model.

NUMERICAL RESULTS AND DISCUSSION

Calculations with this model have demonstrated its ability to qualitatively simulate several important phenomena [4], including: 1) the complex dependence of pit initiation rate on T , 2) the effect of E_{app} on the distribution of pit depths, and 3) the effect of a changing environment on the evolution of the pit depth distribution. One particular simulation that brought valuable insights into modeling pitting of HLRW containers concerned the effect of $[Cl^-]$ on pit growth. Figure 1 shows the results of a Monte Carlo simulation in which both the median pit depth, $\langle d \rangle$, and the maximum pit depth, d_{max} , are plotted as a function of $[Cl^-]$. The logarithmic dependence of $\langle d \rangle$ on $[Cl^-]$ with a slope of 0.5 follows directly from eqn. (11) with $C_4 = 0.5$ for consistency with the data of Herbsleb and Engell [10] for iron. However, d_{max} is independently predicted to be larger at low $[Cl^-]$ than would be expected from a simple extrapolation of the behavior at high $[Cl^-]$. Although no data are available to test this prediction, it may have important implications for modeling the performance of HLRW containers because the deepest pits are of chief concern. If true, this prediction means that extrapolating accelerated test data, gathered using concentrated environments, to the more benign conditions expected in the repository may require stochastic models such as those explored in this study.

As stated earlier, the container environment likely will change during the lifetime of the repository. The stochastic model can account for these changes simply by re-computing the stochastic parameters at each time step based on the current environment using eqns. (8)–(11). These updated parameters are then used to control the birth, death and growth of pits during that time step. An example of how this capability could be used to predict the distribution of pit depths for a plausible HLRW container environmental history has been presented elsewhere [4]. In this paper, the capability to model the effects of a changing environment are demonstrated by simulating the potentiodynamic “sweep” experiment commonly used to determine the pitting potential [13]. This example also demonstrates one way in which standard experimental data could be used to determine whether eqn. (8a) or (8b) is appropriate for a given material.

Figure 1. The median and maximum pit depth (arbitrary units) predicted by the stochastic model as a function of the chloride ion concentration (arbitrary units).

In the potentiodynamic experiment, E_{app} typically is swept from a low value, E_o , toward higher values at a constant velocity, v :

$$E_{app} = E_o + vt, \quad (12)$$

where t is time. The potential at the time the first pit is detected is designated as the pitting potential, E_p . As discussed in detail by Shibata and Takeyama [3,14,15], the stochastic theory of pitting predicts that E_p is actually a distributed quantity for any given v . From a simple algebraic stochastic theory based on birth processes only, Shibata and Takeyama [14,15] deduced the most probable value of the pitting potential, $\bar{E}_p$, as a function of v . The form of this relationship depends on the equation relating λ and E_{app} , (1a) or (1b): using eqn. (1a) leads to

$$\bar{E}_p = (v/\alpha)^{1/2} + E_c, \quad (13a)$$

while eqn. (1b) leads to

$$\bar{E}_p = [1/(\alpha \beta)] \ln(v/\alpha). \quad (13b)$$

Thus, a plot of $\bar{E}_p$ vs. $v^{1/2}$ will yield a straight line if eqns. (1a), (8a) and (13a) are correct, and a plot of $\bar{E}_p$ vs. $\log(v)$ will yield a straight line if eqns. (1b), (8b) and (13b) are correct.

Since the Monte Carlo model computes the generation of a stable pit using the concepts of embryo death and a critical embryo age in addition to embryo birth, the relationships between $\bar{E}_p$ and the embryo birth probability, λ , are more complex than that assumed for deriving eqns. (13). Thus, it is necessary to determine if the $v^{1/2}$ and $\ln(v)$ relationships will be predicted by the Monte Carlo model. If so, then the decision of which form of eqn. (1), and thus eqn. (8), to use for a particular material-environment system can be made from standard potentiodynamic experimental data.

To test this hypothesis, a series of simulations was performed in which the applied potential was varied according to eqn. (12). A particular value of v was chosen and a simulation was performed until the first stable pit was generated. The value of E_{app} at this time step, eqn. (12), was set equal to E_p . This process was repeated with different random number "seeds" [4] to produce 100 separate E_p values for that particular v . A histogram of these E_p values was generated, a smooth curve approximation was made, and the E_p value corresponding to the peak in this curve was designated as $\bar{E}_p$. Following Shibata [3], the median pitting potential, $\langle E_p \rangle$, was also calculated. This process was repeated for different values of v , all other input parameters remaining constant, so plots of $\bar{E}_p$ and $\langle E_p \rangle$ vs. $v^{1/2}$ and $\log(v)$ could be constructed.

The results of such a numerical "experiment" are given in Fig. 2 for the case in which eqn. (8a) was used with $B_I (= E_c) = 0.002$ V; E_o in eqn. (12) was set equal to 0.003 V. The median pitting potential clearly exhibits the $v^{1/2}$ dependence predicted by eqn. (13a) for the simple birth-only model. Interestingly, similar Monte Carlo simulations by Shibata [3] showed a $v^{1/2}$ dependence only at high sweep velocities. The $\bar{E}_p$ results in Fig. 2 show somewhat more scatter than for $\langle E_p \rangle$ but also exhibit the linear dependence on $v^{1/2}$. Using linear regression analysis, a straight line was fit to the $\bar{E}_p$ data and the intercept at zero velocity was calculated to be 0.00208 V. The intercept predicted by eqn. (13a) is $E_c = B_I = 0.002$ V, which is only 4% lower than that predicted by the Monte Carlo model. This suggests that the constant B_I in eqn. (8a) could be determined using potentiodynamic data. Also in agreement with the simple algebraic theory, eqns. (13), plots of $\langle E_p \rangle$ and $\bar{E}_p$ vs. $\log(v)$ were not linear.

Figure 3 presents the results of similar Monte Carlo calculations in which eqn. (8b) was used. In this case, the complex behavior of the Monte Carlo model is apparent. The logarithmic behavior predicted by the birth-only model, eqn. (13b), is exhibited only over a limited range. However, plotting these results as a function of $v^{1/2}$ does not yield linear behavior, so the logarithmic dependence of pitting potential on E_{app} would appear to provide a

better description of these results. Therefore, based on the results in Figs. 2 and 3, it appears that potentiodynamic sweep data may be used to determine whether the linear or exponential form of eqn. (8) should be applied for a particular material–environment system. Of course, additional exploration using a wide variety of input parameters is necessary before this hypothesis can be verified.

Figure 2. Monte Carlo model predictions of the most probable pitting potential, $\bar{E}_p$, and the median pitting potential, $\langle E_p \rangle$, as a function of $v^{1/2}$.

Figure 3. Monte Carlo model predictions of the most probable pitting potential, $\bar{E}_p$, and the median pitting potential, $\langle E_p \rangle$, as a function of $\log(v)$.

CONCLUSIONS

A stochastic model has been presented which simulates the effects of electrochemical potential, chloride ion concentration, and temperature on the aqueous pitting corrosion behavior

of high-level radioactive-waste container materials. The Monte Carlo computer model is based upon the "birth and death" stochastic theory of pitting. The expressions relating the controlling stochastic parameters to the environmental variables were phenomenologically derived from a variety of experimental data. Though simple approximations, these equations are sufficiently reasonable physically so that the potential usefulness of this approach could be demonstrated.

Two examples of the model's capabilities have been presented. First, it is predicted that the maximum pit depth is larger at low chloride ion concentrations than would be expected by extrapolating results from concentrated solutions. This prediction suggests that the extrapolation of accelerated test data, gathered using concentrated environments, to the more benign conditions expected for the waste containers may require a stochastic model. The second example demonstrates the capability of the model to predict the effects of a changing environment by simulating the potentiodynamic "sweep" experiment used to determine the pitting potential. These results suggest that data from such experiments could be used to determine whether a linear or exponential dependence of the pit embryo birth probability on the electrochemical potential should be employed for a given material-environment system.

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