MODELING PITTING CORROSION DAMAGE OF
HIGH-LEVEL RADIOACTIVE-WASTE CONTAINERS,
WITH EMPHASIS ON THE STOCHASTIC APPROACH

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ABSTRACT

Recent efforts to identify methods of modeling pitting corrosion damage of high-level radioactive-waste containers are described. The need to develop models that can provide information useful to higher level system performance assessment models is emphasized, and examples of how this could be accomplished are described. Work to date has focused upon physically-based phenomenological stochastic models of pit initiation and growth. These models may provide a way to distill information from mechanistic theories in a way that provides the necessary information to the less detailed performance assessment models. Monte Carlo implementations of the stochastic theory have resulted in simulations that are, at least qualitatively, consistent with a wide variety of experimental data. The effects of environment on pitting corrosion have been included in the model using a set of simple phenomenological equations relating the parameters of the stochastic model to key environmental variables. The results suggest that stochastic models might be useful for extrapolating accelerated test data and for predicting the effects of changes in the environment on pit initiation and growth.

Preliminary ideas for integrating pitting models with performance assessment models are discussed. These ideas include improving the concept of container "failure", and the use of "rules-of-thumb" to take information from the detailed process models and provide it to the higher level system and subsystem models. Finally, directions for future

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work are described, with emphasis on additional experimental work, since it is an integral part of the modeling process.

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List of Symbols

<u>SYMBOL</u>	<u>MEANING</u>
a	Constant in eqn. (12)
A	Constant in eqn. (5)
A_{cell}	Area of one cell in a Monte Carlo simulation
A_1 to A_4	Constants in eqns. (14) - (17)
b	Constant in eqn. (13)
B_1 to B_5	Constants in eqns. (14) - (17)
C_1 to C_4	Constants in eqns. (14) - (17)
$[Cl^-]$	Chloride ion concentration
d	Pit depth
D	Pit depth growth increment
d_{max}	Maximum pit depth
$< d >$	Median pit depth
E_{app}	Applied or corrosion potential
E_c	Critical potential for pit initiation
E_{crit}	Critical potential for pit growth
E_o, E_1	Constants in eqn. (18)
k_1 to k_4	Constants in eqns. (9) and (10)
K_o, K_1	Constants in eqn. (19)
N	Number of cells used in a Monte Carlo simulation
$< n_{pits} >$	Median number of stable pits
p	Constant in eqn. (5)
Q_λ	Activation energy for pit embryo birth
Q_μ	Activation energy for pit embryo death
Q_τ	Activation energy for pit embryo survival
Q_γ	Activation energy for pit growth

R	Universal gas constant
t	Time
Δt	Computer time step size
T	Temperature
T_{∞}, T_0, T_1	Constants in eqn. (20)
u	Age of stable pit
α, β	Constants in eqn. (7)
γ	Stable pit growth probability
Γ	Average stable pit growth rate (measured)
λ	Pit embryo birth probability
Λ	Pit embryo generation rate per unit area (measured)
λ_0, λ_1	Constants in eqn. (4)
μ	Pit embryo death probability
M	Pit embryo death rate (measured)
τ_c	Critical age to form a stable pit
T_c	Critical age to form a stable pit (measured)
$< \tau_{ind} >$	Median induction time

1. INTRODUCTION

The Yucca Mountain site in Nevada currently is being evaluated by the U. S. Department of Energy for location of a potential geological repository for the storage of high-level radioactive waste, including spent fuel. Prior to emplacement in the repository, the waste will be sealed in high-level radioactive-waste (HLRW) containers, which were required to provide "substantially complete" containment of radionuclides for at least 300-

1000 years under NRC regulation 10CFR60 [1]. It is not yet clear whether this requirement will be maintained under changes called for in the National Energy Policy Act of 1992. However, it seems likely that long-term projection of container behavior will continue to be desirable, if not required. Because these containment times are well beyond those for which experimental data can be collected, the design and analysis of the containers will depend extensively on the results of model calculations.

One area in which model calculations will be crucial is in predicting degradation of the containers by localized corrosion [2]. In particular, modeling aqueous pitting corrosion, the focus of this report, is important for several reasons. (1) Although current efforts are directed toward study of repository heat loading sufficient to keep the waste packages dry for very long times, they will eventually cool to below the boiling point. This makes the presence of liquid water possible, which in turn will make possible aqueous-phase corrosion. (2) Pitting corrosion shares common mechanistic features with other forms of localized corrosion. For example, the growth of pits is very similar to crevice corrosion [3]. Therefore, much can be learned about localized corrosion in general by studying aqueous pitting corrosion. (3) Aqueous pitting corrosion is probably a "worst case" situation and may significantly affect the design of the containers. (4) Re-fluxing of vadose water on the container surface could result in the formation of concentrated electrolytes that promote pitting. Radiolysis of the water may exacerbate this problem [2].

The purpose of this report is to describe recent efforts to establish methods of modeling pitting corrosion that could be used to predict the behavior of HLRW containers. First, the specific objectives of the work are outlined and a general strategy for achieving these objectives is described. The strategy involves investigating both mechanistic/deterministic and phenomenological/stochastic approaches, as well as studying ways in which to integrate the pitting models with the performance assessment models for the entire waste package. To date, the focus has been upon the phenomenological/stochastic approach [4,5], so the majority of this report describes these efforts. In

addition, some preliminary ideas for integrating the pitting models with higher level waste package performance assessment models are discussed, and directions for future work are proposed.

2. OBJECTIVES

The task of modeling localized corrosion of HLRW containers is an ambitious one. First, the materials and environments have not been completely specified, making it difficult to identify precise mechanisms and to categorize them in terms of their likely severity. In addition, the recent paper by Farmer *et al.* [2] demonstrates that there are a large number of possible localized corrosion mechanisms, some of which are not well understood. Given the size of the problem and limitations in resources and personnel, the need to prioritize and focus the modeling effort was deemed to be critical. Therefore, it was decided to concentrate on modeling of pitting corrosion, since pitting poses the most likely threat to the containers. Furthermore, it was decided that aqueous, instead of atmospheric, pitting models should be the focus of near term efforts. Models for austenitic alloys would initially receive the most attention and microbiological corrosion would not be specifically treated at present. Later, as more resources become available, the scope of the modeling effort would broaden.

Pitting corrosion has been studied extensively, and a large number of models have been developed based on various approaches [2]. In selecting a particular approach for use in the present study, consideration first was given to the objective of pitting corrosion modeling for predicting damage to HLRW containers. This objective is to provide useful quantitative input to higher level models that will predict the performance of the waste package and ultimately the repository as a whole. Figure 1 graphically represents the relationship between detailed mechanistic, or "process", models, such as pitting models, and the higher level performance assessment (PA) models. Obviously, the goal is to produce a total system model that predicts the performance of the entire repository. By

necessity, this model (or set of models) will contain few, if any, details regarding the myriad of specific processes that could lead to radionuclide release from the repository. The details are found in the process models, which treat the specific damage and release mechanisms, and form the foundation of the entire modeling effort. The process models are only useful, however, if they support the higher level models. One key to the success of the overall approach is in "distilling" the detailed information from a lower level model so that it can be used in a higher level model containing much less detail. Also depicted in Fig. 1 is that information regarding uncertainties in the predictions comes from the detailed models and is passed upward to the higher levels. Conversely, the sensitivity of the system response to particular processes or uncertainties in predictions comes from the higher levels and is passed downward. This, of course, suggests an iterative approach to developing the entire system of models.

Figure 2 gives a simple example of how models at different levels might interact for the case of a pitting model. First, the subsystem model provides information about the container environment and its variations. The aqueous pitting model uses this information to predict: (1) the time required for the first pit to breach a container wall, (2) the number of subsequent breaches as a function of time, and (3) the increase in size of these through-wall defects. (The latter will require models other than those studied to date, which predict only the nucleation and growth of pits.) These predictions, including uncertainties in results, must be made for a variety of environmental conditions, which may change during the lifetime of the containers. The predictions of the pitting model are then passed to the subsystem model, either as absolute quantities or as approximate "rules-of-thumb", as discussed in Section 5.

Next, we consider the pitting model itself. Many existing models predict critical pitting potentials or electrochemical conditions within the pit, without giving specific predictions of pit depth as a function of time [2]. These models are inadequate for the purpose of providing the PA models with useful information. Models that compute the

pitting corrosion "damage function" [6], however, do provide information useful to higher level models. Specifically, the expected time required for the first pit to penetrate a container and the subsequent increase in the number of through-wall pits can be determined from these results. The pitting corrosion damage function is illustrated schematically in Fig. 3, and is simply a plot of the number (or frequency) of pits at a particular depth vs depth [6]. The damage function is computed for various exposure times assuming that the metal being pitted is infinitely thick. These curves then can be compared with the actual wall thickness of the HLRW container, as shown in Fig. 3. The predicted time required for the first pit to penetrate the wall is that at which the computed damage function first intersects the line corresponding to the wall thickness (t_2 in Fig. 3). At longer times, the *number* of pits penetrating the container wall is proportional to the area under the damage function curve for pit depths greater than the wall thickness (the shaded area under the t_3 curve). Note that the calculated *depths* of through-wall pits have no physical significance, since a pit cannot have a depth greater than the wall thickness.

In summary, the major objective of the work reported here was to identify models capable of computing the pitting corrosion damage function. These results eventually would provide predictions of the expected time required for the first pit to breach the container and the subsequent increase in the number of pits penetrating the container with increasing time. These quantities could then be passed to a higher level PA model for analysis of the effects of HLRW container pitting on waste package performance. Other objectives were to begin exploring ways in which to integrate such models with higher level PA models, to begin developing an overall strategy for pitting corrosion modeling, and to identify areas for further study.

3. STRATEGY

Based on the objectives described in the preceding section, a preliminary strategy for modeling the degradation of HLRW containers by aqueous pitting corrosion was

developed. Beginning with the report by Farmer *et al.* [2], a critical review of existing models would be performed. Emphasis would be placed on identifying models that can quantitatively predict the depth or depth distribution of pits as a function of time and environmental conditions. The initial review of existing models has been completed. Interestingly, there are very few models that provide a means of predicting the distribution of pit depths as a function of time and environment. The most promising models appear to be those of Okada [7], Macdonald *et al.* [8-11] (both mechanistic/deterministic) and Williams *et al.* [12,13] (phenomenological/stochastic). As discussed in Section 4, the models of Williams *et al.* have been chosen for prototype calculations, which are the focus of this report. Work also began with the mechanistic models of Macdonald *et al.* [8-11], but lack of resources forced this effort to be postponed.

Following the identification of a small number of promising models, prototype calculations would be performed to establish the strengths and weaknesses of each. As indicated above, two fundamentally different approaches exist for modeling pitting. The first is the mechanistic, or deterministic, approach, in which the model is based directly on a set of particular mechanisms for pit nucleation and growth. An accurate and complete mechanistic model would provide the best possible basis for the extrapolation of laboratory data to the expected service times and environments. However, it is unclear whether a purely mechanistic model with the required accuracy and generality can be developed in a timely manner; the search for such a model has been in progress for several decades and remains the subject of debate. In addition, it is unlikely that detailed mechanistic models for each of the myriad container degradation modes [2] can be used directly in the waste package PA codes, as suggested in Section 2. More likely, the knowledge gained from mechanistic studies will be "distilled" into less detailed models. Therefore, phenomenological models with a sound physical basis would be explored as one way in which to provide useful predictions while limiting detail. The stochastic pitting models described in Section 4 fall into this category.

Following the prototype calculations, one or two models would be chosen for full analysis and development. At this point, quantitative predictions of pitting corrosion damage of HLRW containers would be made. Simultaneous to the development of pitting models, methods for integrating them with system or subsystem PA models would be considered. This effort would require interaction with experts in performance assessment on a regular basis.

4. STOCHASTIC PIT INITIATION AND GROWTH MODELS

Based on the results of the literature review, the stochastic approach appeared to be promising for modeling pitting corrosion in a way that would provide valuable information to the waste package PA models. The purpose of the research described here was to explore Monte Carlo implementations of stochastic pitting models and to evaluate their utility in predicting the performance of HLRW containers. Efforts began based on the stochastic pit initiation theory of Williams *et al.* [12]. Improving this model and extending it to pit growth then were explored, with emphasis upon simulating the evolution of the damage function (Fig. 3). Finally, a set of simple illustrative equations for simulating the influence of environment on pitting was developed and included in the Monte Carlo model. Within the context of the stochastic approach, the capability to model environmental effects has not received much attention but is critical to predicting the pitting degradation of HLRW containers. Overall, the objective of this research was to develop modeling "tools" based on the stochastic approach. Using these tools, largely qualitative predictions of pitting behavior were made to determine whether or not stochastic models are potentially useful in modeling pitting corrosion damage of HLRW containers, and to identify areas for further study.

4.1 Stochastic Pit Initiation

Within the past decade, experimental evidence has mounted that the nucleation of corrosion pits is a stochastic process. Shibata and Takeyama [14] were the first to show that the critical potential necessary to induce pitting and the "induction" time elapsed before pits become observable are both statistically distributed quantities. For example, Fig. 4 presents their data showing the distribution of induction times for 72 (ostensibly) identical type 304 stainless steel specimens subjected to identical conditions. The data exhibit a wide distribution of induction times, suggesting that pit initiation occurs stochastically. Additional evidence that pit initiation is a stochastic process has been provided by observations of fluctuations in the electric current vs time response prior to the emergence of macroscopic pits. These fluctuations have been attributed to randomly occurring local passivity breakdown and repassivation events that are the precursors to stable pit formation [12,13,15,16].

Experimental observations like those just described have led to the development of several stochastic pit nucleation models [12,14,15,17,18], with pit growth also being treated stochastically in one case [15]. These models are phenomenological but may be viewed as "mechanistically-inspired" since they have been successfully linked with the accepted electrochemical theories of pitting [13,17-20]. In most of the stochastic models, small fluctuations in the local conditions (*e.g.* solution chemistry, fluid flow rate, surface topography, surface metallurgy) are envisioned to cause local breakdown of the passive 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", results. Once an embryo reaches a critical size or age, however, it becomes a "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.

Some of the stochastic models have been developed using algebraic formulations [12,14,18]. Shibata [17] recently noted, however, that "Monte Carlo" models provide a

microscopic or mechanistic view that is lacking in the algebraic formulations, and may improve our understanding of pitting. Therefore, in the present study, Monte Carlo[†] computer codes have been written based on the stochastic model published by Williams *et al.* [12]. These codes establish a unit area that is divided into individual "cells" to represent a metal surface in contact with an aggressive environment. During each time step, a random number between 0 and 1 is generated for every cell without an embryo or stable pit. If this number is less than the birth probability, λ , a pit embryo is placed in that cell; otherwise the cell remains empty. Physically, λ corresponds to the probability that, over the area of one cell in a unit time, the local conditions will cause the passive film to break down, thereby initiating a microscopic pit embryo. Experimentally, these unstable pits result in electrical current transients that can be measured [12,13,16]. Thus, a pit embryo generation rate per unit area, Λ (cm⁻² s⁻¹), can be determined. Methods of measuring Λ are described by Williams *et al.* [12,13], and include the counting of peaks in the current transient. The birth probability used in the computer code is related to the measured rate by:

$$\lambda = \Lambda A_{cell} \Delta t \quad (1)$$

where Δt is the time step size in (s), and A_{cell} is the area of one cell. Thus, λ is proportional to the time step size and inversely proportional to the number of cells, N , since A_{cell} is proportional to $1/N$.

For each cell with an unstable pit embryo present, another random number is then generated. If this number is less than the death probability, μ , the embryo dies and is removed from that cell. The death probability corresponds to the probability that a specific pit embryo, or breakdown in the passive film, will repassivate during a unit time. Pit embryo death has been linked physically, for example, with a reduction in the hydrodynamic boundary layer thickness, which causes a loss of the local concentration

[†] The term "Monte Carlo" is used here in its broadest sense: any model that makes use of random numbers in a calculation that has the structure of a stochastic process [37].

excursions needed to support the pit embryo [13]. Again, μ is related to a measurable pit embryo death rate:

$$\mu = M \Delta t \quad (2)$$

where M is the measured rate in (s^{-1}). Williams *et al.* [13] have shown that the analysis of current-time transients and the resulting spectral power density could be used to obtain M experimentally.

The "age" of each surviving embryo, *i.e.* the number of time steps it has survived since birth, is incremented at each step and compared with the critical age, τ_c . If the age of an embryo equals τ_c , a stable pit is formed in that cell and is present for the remainder of the simulation. Physically, the critical age can be related to the ratio of the minimum stable pit depth to the velocity of pit embryo propagation [13]. The minimum stable pit depth is related to the surface roughness and the thickness of the hydrodynamic boundary layer, and the velocity of propagation depends on the electrochemical potential, aggressive ion concentration, and the nature of the alloy. Like the other pit initiation parameters, τ_c can be related to an experimentally measured quantity:

$$\tau_c = T_c / \Delta t \quad (3)$$

where T_c is the measured critical age in (s). T_c can be measured, for example, as the time of first passage through a pre-defined electrical current level [12,13].

The stochastic pit initiation process described in the preceding paragraphs is repeated for each time step in the simulation, with λ , μ , and τ_c being constant throughout the simulation [12]. The growth of the stable pits with time was not specifically treated by Williams *et al.*, so in the present study a simple model first was employed; the stable pit size was assumed to increase linearly with time. Other models are examined in Section 4.2.

The results of the Monte Carlo model can be displayed graphically in a simple way by representing *stable* pits as squares on the unit plane, where each square has a linear dimension proportional to the computed size of the corresponding pit. Figure 5 gives such

a diagram, and demonstrates the capability of the model to represent the appearance of randomly arranged pits of various sizes. Qualitatively, Fig. 5 is similar to the micrograph of a pitted 316 stainless steel specimen presented by Mola *et al.* [15].

More quantitative conclusions can be drawn by comparing the induction time distribution computed by the Monte Carlo model, Fig. 6, with the data in Fig. 4. To produce Fig. 6, 75 separate simulations were performed with the stochastic parameters given in the figure, where N is the number of cells used in each simulation. (All the input parameters used in this and subsequent simulations are given in the Appendix.) These parameters were chosen arbitrarily, so quantitative agreement with Fig. 4 is not expected. Qualitatively, however, the two distributions are similar. Specifically, the distribution in Fig. 6 is properly skewed toward small induction times, with a long "tail" at large induction times. This shape appears to be common experimentally [14,19,21].

Rather than providing histograms of induction times, experimental data of induction time distributions often are reported using a "survival probability plot" [13,14,17]. This plot gives the logarithm of the survival probability, *i.e.* the probability that a stable pit will *not* appear, as a function of exposure time. Figure 7 shows such a plot with the data of Williams *et al.* [13] given as solid circles, results of their algebraic stochastic theory given as a solid line, and "x"s denoting the results of the Monte Carlo model described above, "PIGS1" (*P*it *I*nitiation and *G*rowth *S*tochastic model no. 1). Although there is variability in the PIGS1 results, Fig. 7 shows that the Monte Carlo model is consistent with the algebraic theory upon which it was based. The data, however, are consistent with these models only for moderate exposure times. After long exposures, the data show a decrease in the magnitude of the slope of the survival probability curve that is not simulated by the models.

In the model proposed by Williams *et al.* [12], it was assumed that the stochastic parameters (λ , μ and τ_c) are single-valued constants. As acknowledged by these investigators, the data in Fig. 7 suggest that this assumption is incorrect. This conclusion

is supported by similar data [14,17,18] showing that the slope of the survival probability plot decreases at long times for a variety of alloys. Williams *et al.* [13] suggested that the stochastic model might simulate this behavior if λ , μ and τ_c were distributed, rather than single-valued, quantities. Another approach is to assume that λ , μ , and τ_c are single-valued but that λ decreases with time. Gabrielli *et al.* [22] cited two possible causes for such a decay in birth probability: (1) an exhaustion of discrete sites for pitting and (2) an increase in the resistance of the passive film to pitting, *e.g.* by thickening. The first possibility forms the basis for the pit initiation model of Mola *et al.* [15]. With possible foundation in either cause, Shibata [23] chose to simulate pit embryo birth as a Poisson process, *i.e.* λ decreases exponentially with time.

Following Shibata's work [23], another Monte Carlo code, "PIGS2", was written in which the pit embryo birth probability decays according to the expression:

$$\lambda = \lambda_0 \exp(-\lambda_1 t) \quad (4)$$

where t is time and λ_0 and λ_1 are constants. Calculations of the survival probability using this model are given as "+"s in Fig. 7 for comparison with the results of PIGS1, in which λ was constant. Both models adequately simulate the data for short times, but PIGS2 more accurately describes the data for long times because the decay in λ decreases the probability for pit embryo formation after long exposures. Results such as these suggest that stochastic models may provide valuable insights into the mechanisms of pitting.

4.2 Stable Pit Growth

The initiation of pits is of no consequence unless they grow to a depth that affects the ability of the HLRW container to prevent the release of radionuclides. This section, therefore, explores the important problem of stable pit growth, where "stable" refers to any permanent pit on the metal surface. As discussed in Section 2, emphasis is placed on

simulating the evolution of the pitting corrosion damage function (Fig. 3), since this can provide valuable information to the repository system PA models.

Figure 8 presents data of Nathan and Dulaney [24] showing the evolution of the damage function with increasing exposure time for aluminum in tap water. The pit depth distributions are bimodal. The first branch has a backwards "J" shape and consists of small pits that grow slowly and are therefore of little concern. In addition, this branch of the distributions is not universally observed [25-27]. For example, Fig. 9 shows the data of Strutt *et al.* [25], in which the number of pits at small depths decreases to zero after some time. The branch of the distributions in Fig. 8 at larger depths is commonly observed and has five key attributes: (1) there is a peak in the distribution at intermediate depths, (2) this peak moves to larger depths as time increases, (3) the height of this peak is smaller at long times than at short times as the distribution broadens somewhat, (4) the number of pits at small depths decreases for long exposure times, and (5) the distribution becomes slightly skewed toward small depths as the exposure time increases. Similar behavior is evident in Fig. 9. The fourth attribute is particularly evident in Fig. 9, and is most clearly seen in Fig. 8 for pits of a depth just below 200 μm . This decrease in the number of small pits with exposure time implies that the pit initiation rate decreases with time, consistent with the decay in λ discussed in the previous section. The decrease in λ also would explain the third attribute, which suggests that the total number of pits ultimately saturates.

In order to simulate these experimental pit depth distributions, stable pit growth must be simulated in the stochastic model in addition to pit nucleation. To date, only Mola *et al.* [15] have specifically treated stable pit growth in the context of a stochastic model. Unfortunately, they did not present damage function predictions which could be compared with the data in Figs. 8 and 9. In the present investigation, the growth of stable pits has been modeled in a way that the damage function evolution could be simulated. The

immediate goal of this effort was to qualitatively simulate the five previously listed attributes of the experimental distributions.

Modeling of stable pit growth began by making the assumption that, once a stable pit forms (*i.e.* an embryo survives for a number of time steps equal to the critical age, τ_c) its depth increases continuously with time. Using the simple linear growth model produces a uniform random distribution of pit depths. As time increases, the distribution remains uniform with the maximum pit depth and the number of pits at each depth increasing with time. These results are inconsistent with the observed behavior, Figs. 8 and 9. In hopes of improving these predictions, a more realistic stable pit growth law was taken from the work of Janik-Czachor and Ives [26] and has the form:

$$d = A u^p \quad (5)$$

where d is the pit depth, u is the age of the stable pit, and A and p are constants for a given material and environment. For $p < 1$ (expected from various theories and experiments [3]), this model produces damage functions that become increasingly skewed toward large pit depths as time increases. This behavior is not supported by the experimental data in Figs. 8 and 9. In addition, for both the linear and power-law ($p < 1$) growth models, use of a pit nucleation probability that decays with time, eqn. (4), also produces damage functions skewed toward large depths.

The poor agreement between the shapes of the damage functions resulting from monotonic growth models and the observed shapes may imply that stable pits do not grow continuously. Instead, growth of stable pits may follow a "start/stop/start" sequence, perhaps due to a succession of growth, death and renucleation events [13]. Alternatively, a lack of available reactants, such as oxygen or aggressive ions, could cause some pits to permanently stop growing after reaching a certain depth while others continue to grow [28]. A stochastic approach to stable pit growth may be appropriate in either case.

In the present study, the effects of stochastic stable pit growth on the damage function evolution were studied using a simple approach: growth of a stable pit during a particular time step occurs only if a randomly generated number between 0 and 1 is less than the prescribed growth probability, γ . Physically, γ corresponds to the probability that a pit will grow an increment in depth in an interval of time. Thus,

$$\gamma = \frac{\Gamma \Delta t}{D} \quad (6)$$

where Γ is an average growth rate with units of (cm s^{-1}), and D is the size of the depth increment in (cm). The value of Γ could be measured by fitting experimental data for the evolution in the distribution of pit depths. As suggested in the previous paragraph, the mechanistic significance of γ could stem from a variety of causes, and careful experiments to determine these causes are warranted. Finally, unlike the approach of Mola *et al.* [8], γ is assumed to be constant in the present model, and pits are assumed to be hemispherical.

An example of the simulated damage function evolution resulting from this model is given as a series of histograms in Fig. 10. For short times (10 steps) the distribution is narrow, with a large number of pits at low depths. As time increases, the total number of pits increases (40 steps) and the peak in the distribution occurs at an intermediate depth. The number of pits at very low depths is now less than at shorter times. At long times (100, 125 steps), the number of pits stays fairly constant and there are few (if any) pits at low depths. The distribution also begins to broaden and the number of pits at the peak of the distribution is less than at shorter times. The depth at which the peak occurs continuously increases with time. Finally, the distribution at long times is not significantly skewed towards large depths (as it was using the continuous growth laws). As listed earlier, the experimental distributions in Figs. 8 and 9 have similar attributes, suggesting that the assumptions of decaying birth probability and stochastic stable growth may be reasonable.

Following from the discussion of Fig. 3 in Section 2, predictions like those in Fig. 10 could be useful for repository system PA. For example, if the HLRW container wall thickness was 32 (arbitrary units), Fig. 10(c) shows that the time required for first penetration of the container is about $100 \Delta t$, where Δt is the time step size. With further exposure to a time of $125 \Delta t$, Fig 10(d) shows that approximately 25 pits will have penetrated a unit area of the container.

4.3 Modeling the Effects of Environment on Pitting

4.3.1 Development of an Illustrative Model

One major purpose of modeling pitting corrosion of HLRW containers 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. Predicting the effects of environment on pitting also will be required to explore container performance for various environmental scenarios, including the expected [2,8] case in which the environment changes with time.

In the context of stochastic pitting models, the goal is to model the environmental sensitivity of the stochastic parameters: λ , μ , τ_c , and γ . Rigorous development of such relationships was beyond the scope of the present study and probably would require considerable experimental work from which to derive the equations. Therefore, simple but physically reasonable expressions have been selected based on a limited amount of available data. 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 environments.

Three important environmental parameters have been included in the illustrative model: applied potential, E_{app} , chloride ion concentration, $[Cl^-]$, and absolute temperature, T . (Note that a potential is intentionally applied in experimental studies. The potential on a HLRW container in a repository would be determined by the corrosion reactions that occur in that environment.) Other variables, such as pH, oxygen concentration and the presence of other ions in solution, would need to be included in a complete analysis. The effects of changes in the availability of reactants to individual pits is another area for future research [28].

Relating the stochastic pit initiation parameters (λ , μ , and τ_c) to E_{app} , $[Cl^-]$, and T was done based on the extensive experimental work of Shibata and co-workers [17,19,21,29], in which these relationships were explored directly. Two different relationships between λ and E_{app} were observed:

$$\lambda \sim \alpha (E_{app} - E_c) \quad (7a)$$

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

$$\lambda \sim \alpha \exp(\beta E_{app}) \quad (7b)$$

where α and β are constants. The death probability was found not to be a function of E_{app} . Further, Shibata showed [21,29] that the temperature dependencies of the pit initiation parameters can be represented by separate Arrhenius expressions:

$$\lambda \sim \exp(-Q_\lambda / RT) \quad (8a)$$

$$\mu \sim \exp(-Q_\mu / RT) \quad (8b)$$

$$\tau_c \sim \exp(+Q_\tau / RT) \quad (8c)$$

where R is the gas constant and the Q_i are the activation energies for each process. The remaining proportionalities were not given explicitly in the work of Shibata, but approximate relationships can be gleaned from the data. From Fig. 4 of [19], a reasonable approximation is:

$$\tau_c \sim \exp(-k_1 \cdot E_{app}) \quad (9)$$

where k_1 is a constant. From the data presented in Fig. 8 of [19] it is reasonable to assume:

$$\lambda \sim \exp(k_2 \cdot [\text{Cl}^-]) \quad (10a)$$

$$\mu \sim \exp(-k_3 \cdot [\text{Cl}^-]) \quad (10b)$$

$$\tau_c \sim \exp(-k_4 \cdot [\text{Cl}^-]) \quad (10c)$$

where the k_i are constants.

Experimental data such as those of Shibata for the pit initiation parameters are not directly available for the stochastic pit growth probability, γ . Clearly, additional experimental effort is needed in determining the effects of environment on pit growth. For the purposes of illustration, however, we follow the work of Broli *et al.* [30], Herbsleb and Engell [31], Szklarska-Smialowska and Janik-Czachor [32], Heimgartner and Böhni [33], Böhni [34], and Janik-Czachor [27].

Based on the data of Broli *et al.* [30], the current density *within a pit* increases as the temperature increases. Assuming an Arrhenius relationship, which is probably an oversimplification, gives:

$$\gamma \sim \exp(Q_\gamma/RT) \quad (11)$$

where Q_γ is the activation energy for pit growth. The data of Broli *et al.* also indicate that γ increases as $[\text{Cl}^-]$ increases. Further, the data of Herbsleb and Engell [31] suggest:

$$\gamma \sim [\text{Cl}^-]^a \quad (12)$$

where a is a constant.

Two different dependencies of γ on E_{app} are suggested in the literature. First, the data of Herbsleb and Engell [31] and the data of Heimgartner and Böhni [33] show that γ is independent of E_{app} . This is consistent with the diffusive transport theory of pit growth, as discussed by Böhni [34]. In the second case, data of Janik-Czachor [27] indicate that the rate of pit growth increases as E_{app} increases. Further, data of Szklarska-Smialowska and Janik-Czachor [32] 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:

$$\gamma \sim (E_{app} - E_{crt})^b \quad (13)$$

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 only to demonstrate the potential usefulness of including environmental dependencies for the stochastic parameters in the stochastic model, it was simply assumed that the separate proportionalities implied in equations (7) - (13) could be directly combined. No synergistic reactions between variables was assumed. Therefore, combining these expressions and using a self-consistent scheme for denoting constants, led to the following empirical expressions for the environmental dependence of the stochastic parameters:

$$\lambda = A_1 (E_{app} - B_1) \cdot \exp(C_1 \cdot [Cl^-]) \cdot \exp(-Q_\lambda/RT) \quad (14a)$$

or

$$\lambda = A_1 \cdot \exp(B_1 \cdot E_{app}) \cdot \exp(C_1 \cdot [Cl^-]) \cdot \exp(-Q_\lambda/RT) \quad (14b)$$

$$\mu = A_2 \cdot \exp(-C_2 \cdot [Cl^-]) \cdot \exp(-Q_\mu/RT) \quad (15)$$

$$\tau_c = A_3 \cdot \exp(-B_3 \cdot E_{app}) \cdot \exp(-C_3 \cdot [Cl^-]) \cdot \exp(+Q_\tau/RT) \quad (16)$$

$$\gamma = A_4 \cdot [Cl^-]^{C_4} \cdot \exp(+Q_\gamma/RT) \quad (17a)$$

or

$$\gamma = A_4 (E_{app} - B_4)^{B_5} \cdot [Cl^-]^{C_4} \cdot \exp(+Q_\gamma/RT) \quad (17b)$$

where the A's, B's, and C's are constants. The expressions for λ , μ and γ allow for probabilities greater than 1.0 (though the computer code limits their values to a maximum value of 1.0). Therefore, the units for the constants in (14)–(17) must be correctly chosen to keep these probabilities less than 1. Finally, the value of τ_c computed from (16) is truncated in the computer code to yield an integer number because time is discretized into steps.

Equations (14) - (17) were included in the Monte Carlo code described in Sections 4.1 and 4.2 so that its ability to simulate the effects of environment on pit initiation and growth could be qualitatively demonstrated [the simulations presented in the next section used only equations (14a) and (17b), in addition to (15) and (16)]. To use this model for quantitative predictions of pitting, the constants in (14)-(17) would need to be evaluated from experimental data similar to those used in establishing the forms of these equations. The scaling constants (A_1 to A_4) would need to be evaluated from measurements of λ , μ , τ_c and γ using techniques described briefly in Sections 4.1 and 4.2. The quantitative evaluation of the constants was not attempted, however, because many of the required data currently are not available, and because the preliminary nature of equations (14)-(17) does not warrant such an effort. Therefore, the constants used in the following examples were simply chosen to illustrate specific capabilities of the model.

4.3.2 Simulations with the Model

In a review of the temperature dependence of pit initiation, Szklarska-Smialowska [35] found considerable variability. Arrhenius behavior was not always observed, and the tendency for pitting was found both to increase and decrease with increasing temperature. In fact, both types of behavior can occur within one material/environment system, as shown by the data in Fig. 11(a) for the critical pitting potential of pure iron. This complex behavior is due to the multiple processes that occur during pitting, each with a different temperature dependence [35].

Since the temperature dependence of each stochastic variable is treated separately in equations (14) - (17), the model is capable of simulating complex temperature dependencies in the pit initiation response. Specifically, an increase in temperature increases λ and μ while decreasing τ_c . The increase in λ and the decrease in τ_c *increase* the tendency for pit initiation as the temperature rises, while the increase in μ *decreases* the tendency for pitting. In addition, even though each equation has the usual Arrhenius term, different activation

energies are assumed for each stochastic parameter. This allows the model to simulate data in which Arrhenius behavior is non-existent or is limited to narrow temperature ranges [35].

The capability of the stochastic model to simulate complex changes in the pit initiation response to changes in T is demonstrated in Fig. 11(b). The current model does not compute critical pitting potentials, so the median induction time, $\langle \tau_{\text{ind}} \rangle$, was chosen as the measure of pitting tendency. To simplify the simulation, Q_τ was given a low value so that τ_c was nearly independent of T , while Q_λ and Q_μ were given larger values to control the simulation. Fig. 11(b) clearly shows that the model is capable of simulating a reversal in the effect of T on the macroscopic pitting response which is qualitatively similar to that shown by the data in Fig. 11(a). This capability results from separately treating the temperature dependence of pit embryo birth and death. Using values for the activation energies different from those given in Fig. 11(b), however, a single trend in pit initiation response with changing T can be simulated over a wide range of T , if desired. Finally, the data and simulations in Fig. 11 indicate that caution is required in designing accelerated tests; increasing T may not necessarily increase pitting rates.

The next example explores the influence of $[\text{Cl}^-]$ in the model and focuses upon pit growth rather than initiation. Figure 12(a) presents data of Herbsleb and Engell [31] for iron, showing the increase in the average pit radius[†] with increasing $[\text{Cl}^-]$ for two different growth times. For both times, the pit radius increases with increasing $[\text{Cl}^-]$ according to a power-law relation with an exponent of about 0.5. Figure 12(b) shows the results of Monte Carlo simulations in which both the median pit depth, $\langle d \rangle$, and the maximum pit depth, d_{max} , were determined as a function of $[\text{Cl}^-]$. In Fig. 12(b), the logarithmic dependence of $\langle d \rangle$ on $[\text{Cl}^-]$ with a slope of about 0.5 follows directly from eqn. (17) with C_4 chosen to be 0.5 for consistency with the data in Fig. 12(a). However, d_{max} is larger at

[†] Herbsleb and Engell defined two radii to describe the geometry of their pits. Such a distinction has not been made in the model.

low $[\text{Cl}^-]$ than would be expected from a simple extrapolation of the behavior at high $[\text{Cl}^-]$. 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 extrapolation of accelerated test data in concentrated environments to the more benign conditions expected in the repository may require stochastic models such as those explored in this study.

As discussed earlier, the pit depth distribution, or damage function is of great interest in modeling pitting corrosion damage of HLRW containers. The next example explores the dependence of the damage function on the applied potential, E_{app} . The data of Janik-Czachor [27] for pitting of iron in buffered chloride solutions are given in Fig. 13(a), where the pit size was measured as the diagonal distance across polyhedrally shaped pits, rather than as the depth. As the applied potential increases (*i.e.* becomes more positive) the total number of pits and their maximum size increase, indicating that the pits grow more rapidly as E_{app} increases. The median pit size also appears to increase with increasing E_{app} . As with the data in Figs. 8 and 9, the distributions tend to be skewed toward small pit sizes. Figure 13(b) shows the results of Monte Carlo simulations in which the applied potential was varied and the effect on the damage function was determined. Equation (4) was used to provide an exponential decay in λ with time for these simulations. Qualitatively, most features of the experimental damage functions are reproduced in Fig. 13(b). As E_{app} increases, the number of pits increases and the median and maximum pit sizes (*i.e.* depths) increase. The need for improvements to the model is apparent, however, because the simulated damage functions are not skewed toward small pit depths in a manner analogous to the pit diagonal distributions in Fig. 13(a). One method of producing more realistic distributions may be to use a growth probability that varies with pit depth. Exploring this possibility is suggested as one area of future research. For the present, however, the results in Fig. 13(b) illustrate the potential usefulness of the stochastic model

for extrapolating accelerated test data and simulating the effect of E_{app} on the damage function.

As stated at the beginning of this section, the container environment certainly 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 and then using these updated parameters to control the birth, death and growth of pits. For example, let the three environmental variables considered here change with time according to the following simple expressions:

$$E_{app} = E_0 - \exp(-E_1 t) \quad (18)$$

$$[Cl^-] = K_0 \exp(K_1 t) \quad (19)$$

$$T = T_\infty + T_0 \exp(-T_1 t) \quad (20)$$

where t is time and E_0 , E_1 , K_0 , K_1 , T_∞ , T_0 and T_1 are constants. These equations were chosen to represent plausible changes in the repository environment. Equation (18) represents an increase in corrosion potential toward an asymptotic limit, as suggested by the calculations of Macdonald and Urquidi-Macdonald [8]. The increasing $[Cl^-]$ given in eqn. (19) represents the concentration of electrolyte that might occur if the container surfaces are alternately wet and dry; the form of the equation is simply illustrative. Equation (20) simulates the expected exponential decay in temperature toward some ambient level, T_∞ [2]. Figure 14(a) shows the behavior of each environmental variable as a function of time using equations (18)-(20).

Modeling the dependence of each stochastic parameter on each of the relevant environmental variables allows the stochastic model to predict some rather complex behavior, even using the simple illustrative equations (14)-(17). The behavior of the stochastic parameters corresponding to the environmental scenario depicted in Fig. 14(a) is shown in Fig. 14(b). The simple monotonic changes in E_{app} , $[Cl^-]$ and T produce complex

changes in the stochastic parameters, particularly λ and τ_c . While eqns. (14)-(20) are illustrative, they are physically reasonable. Therefore, the results of Fig. 14(b) suggest that simple changes in a small number of key environmental variables could cause complicated changes in macroscopic response. Physically-based phenomenological or sound mechanistic models may then be *required* to account for the effects of a changing container environment on pitting degradation.

The effects that the environmental history shown in Fig. 14 have on the damage function evolution are shown in Fig. 15. Initially, a large number of stable pits are nucleated because τ_c is low and λ rises rapidly. These pits do not grow significantly at this point because γ is small. At intermediate times, few new pits are initiated because λ decreases from its peak at $t \approx 15$ and τ_c is increasing. The increase in γ , however, causes the existing pits to grow more rapidly than at short times, leading to the lack of pits at low depths. At long times (115 steps), new pits again initiate because λ increases and μ and τ_c decrease. The pits already present grow at an ever-increasing rate because of the behavior of γ . Given the illustrative nature of the environmental scenario and equations (14)-(17), the details of this simulation are not particularly important. This example, however, demonstrates the potential of the stochastic model to predict the evolution of the damage function under conditions of changing environment. This is a necessary capability of any detailed pitting model to be used in predicting the performance of HLRW containers.

4.4 Discussion

4.4.1 Details of the Stochastic Computer Models

An important issue in stochastic modeling is that of variability in the results. There are two aspects of variability. First, the use of random numbers causes run-to-run variations in the computed results, which mirrors the stochastic nature of the physical problem (*e.g.* Figs. 4,6,7). The amount of variation depends upon the number of

computer runs or experimental samples. Despite this variation, preliminary analyses of the models described here show, for example, that useful median or "expected" values (*e.g.* $\langle \tau_{\text{ind}} \rangle$, $\langle d \rangle$) can be computed if multiple runs are performed for each simulation. As shown in the Appendix, 50–100 individual runs typically were made for each simulation. The variation in median values between separate multi-run simulations was typically less than 10%. For example, ten separate 100-run simulations made with the parameters used to construct Fig. 7 gave a standard deviation in $\langle \tau_{\text{ind}} \rangle$ of only 6.5%. Therefore, it appears that the stochastic models can provide median values of low variability, as well as an indication of the "sample-to-sample" variation in behavior that is characteristic of a stochastic process (Figs. 4,6,7).

The second aspect of variability concerns the sensitivity of the results to small uncertainties in the input parameters – λ , μ , τ_c , and γ . A full sensitivity analysis was beyond the scope of this paper, but semi-quantitative results are given in Table I. The calculated results generally are most sensitive to the value of μ , with the exception of $\langle d \rangle$, which depends mostly on γ . Further, the dependencies of $\langle \tau_{\text{ind}} \rangle$ and $\langle n_{\text{pits}} \rangle$ on λ , μ , and τ_c given in Table I are essentially consistent with those predicted by Williams *et al.* [12] for their algebraic stochastic theory. The sensitivity of the model to uncertainties in the constants in equations (14)-(17) was not studied due to the illustrative nature of these equations.

4.4.2 Stochastic and Mechanistic Modeling Approaches

The stochastic models described in Section 4 are phenomenological, and may be less desirable than a completely mechanistic model from the standpoint of confidently extrapolating accelerated test data. In addition, collection of extensive experimental data will be required for evaluation of the parameters in the stochastic models and their sensitivity to the environment. However, development of these mechanistically-inspired phenomenological models is useful for several reasons. First, as demonstrated in Fig. 15,

they could provide information useful to the waste package PA models, namely evolution of the damage function under arbitrarily complex environmental conditions. Second, individual mechanistic models may be applicable only to a small number of material-environment combinations. Since the container materials and environments have not been specified with certainty, the more general stochastic approach is useful at this point. Third, the stochastic models provide a framework for studying pitting corrosion that could complement the mechanistic approach. For example, the results of this study suggest that the decrease in pit initiation rate with time and the possible stochastic nature of "stable" pit growth deserve further investigation. Conversely, our ever-improving mechanistic understanding of pitting could be instilled in a relatively simple stochastic model [e.g. improving equations (14)-(17)], which may interface with the waste package PA codes better than a set of detailed mechanistic models. Finally, there is now wide agreement that any model of pitting must account in some way for the stochastic nature of the process. The Monte Carlo models provide a natural and insightful means of simulating this aspect of pitting.

5. INTEGRATION WITH PERFORMANCE ASSESSMENT MODELS

As discussed in Section 2, detailed pitting models like those just described are useful only if the information they provide can be used in a higher level performance assessment model. Much still remains to be done in integrating the pitting models with the waste package PA models, but some preliminary ideas are presented in this section.

One current concept of the "failure" of a container is that it immediately goes from a state of completely containing radionuclides to one of non-existence upon failing. Particularly at the "subsystem" level (Figs. 1 and 2), this concept of container failure may need to be refined. A more likely scenario is that different "failures" occur in a single container and that they release radionuclides in different ways (gas or liquid transport) at

vastly different rates, as illustrated in Fig. 16. Upon first penetration of a pit (or crack), the container defect may be large enough to release gas but too small for significant liquid transport. Later, as the defect grows, liquid transport becomes possible. Figures 2 and 3 suggest that the pitting model could be used to predict the number and sizes of failures in a container as a function of time, and pass this information up to the subsystem PA model. (Note that, in order to compute the sizes of specific failures, a model for predicting the growth of through-wall defects would be required in addition to pit initiation and growth models of the type described in Section 4).

In Section 2, mention was made of the need for distilling information from detailed process models to less detailed subsystem and system models (Fig. 1). An example of how this might be accomplished is given in Fig. 17. The approach is to establish approximate "rules-of-thumb" based on calculations with the detailed process models. In the example shown in Fig. 17, models such as the stochastic pitting model are used to predict the time elapsed before the appearance of the first container defect capable of releasing gas, t_1 . Then, through-wall defect growth models would be used to predict the time it takes for such a defect to grow to the size required for liquid transport to occur at a significant rate, t_2 . In the case of Fig. 17, $t_2 \approx 2t_1$, which is established as a rule-of-thumb. The pit and through-wall growth models would then be used to establish an approximate time for which the container no longer provides any significant containment of radionuclides, t_3 . As before, a rule-of-thumb is established, e.g. $t_3 = 10t_1$ in the case of Fig. 17. Once these rules-of-thumb are established using the process models, they are incorporated into the higher level model, which contains no details regarding the degradation process but simulates the *effects* of that process.

6. FUTURE WORK

6.1 Stochastic Models

While the present investigation into stochastic pit initiation and growth models has established some of the tools needed to perform predictions of pitting corrosion that would be useful in the waste package PA, little quantitative validation of these models has been performed (Fig. 7 being an exception). In part, this is due to a lack of available data with which to determine model parameters and compare predictions. Thus, experimental efforts loom as a requirement for further development and testing of the models, particularly the determination of pit depth distributions as a function of time and environment. Furthermore, the results of this investigation suggest that stochastic models might be useful for extrapolating accelerated test data and for predicting the effects of changes in the environment on pit initiation and growth. The validity of such extrapolations will depend, of course, on the accuracy of the equations used to describe the environmental dependence of the stochastic parameters and on the assumption that the stochastic nature of pitting, as well as other physical processes, do not change over the extremely long exposure times. Validating whether the stochastic models provide a predictive capability is an important area for future study, and again will require collecting experimental data.

In addition to these experimental efforts, future research with stochastic pitting models should focus on three areas. First, the stochastic approach to modeling stable pit growth needs to be investigated and perhaps improved. Second, physically-sound methods for simulating the effects of environment on the stochastic parameters need to be established. Although the equations developed in Section 4.3 were adequate for the illustrative purposes of the current study, they clearly must be improved and expanded to include variables and phenomena not treated here. Third, methods to quantitatively determine the model parameters from experimental data need to be explored. Williams *et al.* [13] have developed such methods for the three-parameter pit initiation model; their

work could be used to guide this effort. Once these tasks have been accomplished, quantitative predictions can be made, compared with data, and used to guide improvements to the models.

6.2 Overall Efforts in Modeling Localized Corrosion

As mentioned with respect to the stochastic models, experimental efforts arise as a major need in improving and validating models of localized corrosion. Therefore, it is useful to elaborate on the synergism between experiments and modeling in general. There is sometimes a misconception that modeling is a replacement for experimentation. This is obviously untrue since the constants in the model are determined by experimentation in all but the most fundamental models, and the results of experiments drive the formulation of the model. These and other interactions between experimentation and modeling are schematically illustrated in Fig. 18. In the figure, note how experimental data are required to improve the fundamental theory, to construct a working model, to determine the model parameters, and to test the model. Experimental data also are required for comparison of independent predictions for model validation. Since the need for experimental data is great, one might ask why modeling needs to be performed at all. The advantage of modeling, over just performing experiments alone, comes partially through an increased understanding of the physical processes. In addition, there is a reduction in the amount of experimentation required because not all possible external conditions need to be tested if an adequate model can be developed to interpolate between those conditions that have been tested. Finally, and most importantly in the case of HLRW containers, the models will be used to extrapolate to times and environments that cannot be achieved experimentally.

In addition to the future efforts required to develop the stochastic pitting models and collect experimental data, other long term efforts are needed. First, mechanistic pitting models should be explored, such as those of Macdonald *et al.* [8-11]. Efforts to integrate the pitting models with the waste package PA models also need to be continued.

Quantitative predictions of the pitting corrosion damage function need to be made for candidate container materials under realistic environmental conditions. This includes evaluating the effects of changes in temperature, humidity, water chemistry, *etc.* that may be envisioned to occur during the containment period. These results then must be incorporated into the waste package PA models to make predictions of system performance for different environmental conditions and container materials. Finally, the scope of the localized corrosion modeling effort clearly must broaden. This includes expanding the localized corrosion mechanisms being modeled to encompass, for example: crevice corrosion, microbiological corrosion, and stress corrosion. It also may be necessary to broaden the types of materials being considered to include a variety of metals and nonmetals that may be present in future repository conceptual designs.

7. SUMMARY AND CONCLUSIONS

This report has described recent efforts in establishing methods of modeling aqueous pitting corrosion damage of high-level radioactive-waste containers. The major objective was to identify one or more models that could simulate pitting of these containers in a way that would provide information useful to higher level, less detailed performance assessment models. Models that predict the distribution of pit depths as a function of time, the "damage function", have been identified as part of this requirement.

A preliminary strategy for achieving these objectives has been developed and implementation has begun. The first step was to review the literature for models that can predict the damage function. Mechanistic models have been judged to be important to study, but physically-based phenomenological stochastic models were chosen as the initial focus because they may provide a way to distill the knowledge gained from mechanistic studies into less detailed higher level models.

Phenomenological stochastic models for predicting the degradation of high-level radioactive-waste containers by aqueous pitting corrosion are based on a variety of experimental data demonstrating the stochastic nature of pitting. Monte Carlo implementations of the stochastic theory have resulted in simulations that are, at least qualitatively, consistent with a wide variety of experimental data. The effects of environment on pitting corrosion have been included in the model using a set of simple phenomenological equations relating the parameters of the stochastic model to key environmental variables. The results suggest that stochastic models might be useful for extrapolating accelerated test data and for predicting the effects of changes in the environment on pit initiation and growth. (The validity of such extrapolations will depend, of course, on the degree of confidence that can be placed in the experimental data and in the assumption that all important processes that may occur at long times have been accounted for.) Another key attribute of the Monte Carlo models is that they could provide information useful to the waste package system performance assessment models. Specifically, they can predict the expected time required for the first pit to penetrate a wall of known thickness and the subsequent time-dependent increase in the number of through-wall pits. Therefore, it is concluded that Monte Carlo implementations of stochastic pitting models are potentially useful for predicting the degradation of high-level radioactive-waste containers.

Preliminary ideas for integrating pitting models with performance assessment models have been discussed, and center on improving the concept of container "failure" and the use of "rules-of-thumb" to take information from detailed process models to higher level system and subsystem models. Directions for future work, both with the stochastic models and localized corrosion modeling in general, have been described. The need for additional experimental work was emphasized, since it is an integral part of the modeling process.

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Appendix

This appendix provides the reader with the parameters used to make the computer calculations presented in the figures. The symbols used in the following tables have been defined in the body of the paper, with the exception of several control parameters. To aid in defining these parameters, it is necessary to describe several details of the computer codes. First, the random number generation routine was taken from Press *et al.* [38], and requires a starting “seed” value. This seed value is termed IDUM in the tables below. To provide meaningful results, the computer code must be run multiple times, since the stochastic nature of the model will necessarily result in run-to-run variations. To facilitate this process, a control variable, NRUNS, was established that defines the number of runs to make with the identical stochastic and environmental parameters. For each run, the seed value for the random number generator is incremented to provide the statistically varying results. This was accomplished using IDUM as the seed for the first run, and then multiplying the run number by the variable IMULT to provide the seed for subsequent runs. Finally, the variable NSTEP was used to define the number of time steps in each run. Calculations were made on a Macintosh II computer, with computation times typically about 5 min. for a 50-run simulation using 100 cells and 200 time steps.

Since only qualitative results were desired in most cases, the time step size, Δt , was assumed to be of unit value (*i.e.* 1 s). For Figures 7 and 10, however, Δt was varied so the values of the stochastic parameters had to change accordingly. Following equations (1)–(3) and (6), the variables that change proportionally with Δt are: λ (or λ_0), μ , and γ . The variables that change inversely with Δt are: τ_c and NSTEP.

Table A.1 Input parameters for the environmentally-insensitive simulations.

Constant (units)	Figure 6	Figure 7 * (PIGS1 / PIGS2)	Figure 10 *
N	400	100	100
λ	0.02	6.9×10^{-5} / -----	-----
λ_0	-----	----- / 6.9032×10^{-5}	0.02151
α	-----	----- / 4.624×10^{-4}	0.07296
μ	0.3	0.016	0.3
t_c	15	50	4
γ	-----	-----	0.25
Δt (s)	1	0.1 to 10.0	0.01 to 1.0
NSTEP	50	999 / 1500	125
NRUNS	75	100	10
IDUM	-47	-27 / -7	-7
IMULT	47	27 / 7	7

* Parameters that depend on the time step size are given only for the case of $\Delta t = 1$ s.

Table A.2 Input parameters for the environmentally-sensitive simulations.

Constant (units)	Figure 11(b)	Figure 12(b)	Figure 13(b)	Figures 14-15
A ₁	5.11x10 ¹¹	6.164x10 ¹²	6.164x10 ¹²	6.164x10 ¹²
A ₂	708.	4.856	4.856	4.856
A ₃	25.7	2.7x10 ⁻⁴	2.7x10 ⁻⁴	2.7x10 ⁻⁴
A ₄	-----	2.0x10 ⁻⁴	2.0x10 ⁻⁴	1.0x10 ⁻⁷
B ₁	0.4	0.4	0.4	0.4
B ₃	0.4	0.4	0.4	0.4
B ₄	-----	0.4	0.4	0.4
B ₅	-----	0.5	0.5	0.3
C ₁	1.0	1.0	1.0	1.0
C ₂	1.0	0.2	0.2	0.2
C ₃	1.0	0.2	0.2	0.2
C ₄	-----	0.5	1.1	0.2
Q _λ (kJ/mol)	2.0x10 ⁴	2.27x10 ⁴	2.27x10 ⁴	2.27x10 ⁴
Q _μ (kJ/mol)	5,000	1,600	1,600	1,600
Q _τ (kJ/mol)	100.	750	750	750
Q _γ (kJ/mol)	-----	1.0x10 ⁴	1.0x10 ⁴	1.0x10 ⁴
α	0	0	5.352x10 ⁻²	0
E ₀	1.5	1.5	1.45 to 1.60	1.4
E ₁	0	0	0	0.047
K ₀	0.5	1x10 ⁻⁶ to 2x10 ⁻⁴	0.011	0.01
K ₁	0	0	0	4.65x10 ⁻²
T ₀ (K)	0	48	48	49
T ₁	0	0	0	2.252x10 ⁻²
T _∞ (K)	275 to 380	320	320	320
N	400	400	400	400
NSTEP	1500	100	200	125
NRUNS	75	60	30	50
IDUM	-47	-47	-47	-47
IMULT	47	47	47	47

Notes: For all calculations, $\Delta t = 1.0$ s.

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Table I. Sensitivity of the median induction time, $\langle \tau_{\text{ind}} \rangle$, median number of stable pits, $\langle n_{\text{pits}} \rangle$, and median pit depth, $\langle d \rangle$, to changes in the stochastic parameters.

Model Result	λ	μ	τ_c	γ
$\langle \tau_{\text{ind}} \rangle$	Large λ : Independent Small λ : $\sim 1/\lambda$	Complex: increases rapidly for $\mu > 0.5$	$\sim \exp(\tau_c)$	Independent
$\langle n_{\text{pits}} \rangle$	$\sim \lambda$	$\sim \exp(-\mu)$	$\sim \exp(-\tau_c)$	Independent
$\langle d \rangle$	Nearly independent	$\sim \mu^{-n}$; $n < 1$	Nearly independent	$\sim \gamma$

Figure 1.

**Radionuclide release rate from container
as a function of time.**

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Figure 11.

Figure 12.

Figure 13.

Figure 14a.

Figure 14b.

Figure 15.

Figure 16.

t_1
First pinhole
failure

$t_2 = 2 \cdot t_1$
First failure with
liquid transport

$t_3 = 10 \cdot t_1$
Container no
longer a barrier

Figure 17.

Figure 18.

END

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