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CREVICE CORROSION & PITTING OF HIGH-LEVEL WASTE CONTAINERS: A FIRST STEP TOWARDS THE INTEGRATION OF DETERMINISTIC & PROBABILISTIC MODELS

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ABSTRACT

An integrated predictive model is being developed to account for the effects of localized environmental conditions in crevices on pit initiation and propagation. A deterministic calculation is used to estimate the accumulation of hydrogen ions (pH suppression) in the crevice solution due to equilibrium hydrolysis reactions of dissolved metal. Pit initiation and growth within the crevice is dealt with by either a stochastic probability model, or an equivalent deterministic model. While the strategy presented here is very promising, the integrated model is not yet ready for accurate quantitative predictions. Empirical expressions for the rate of penetration based upon experimental crevice corrosion data should be used in the interim period, until the integrated model can be refined. Both approaches are discussed.

INTRODUCTION

The Engineered Barrier System (EBS) being designed for containment of spent-fuel and high-level waste at the proposed geological repository at Yucca Mountain, Nevada is a two-layer canister. In this particular design, the inner barrier is made of a corrosion resistant material (CRM) such as Alloys 825, 625, C-276 or C-22, while the outer barrier is made of a corrosion-allowance material (CAM) such as carbon steel or Monel 400. Initially, the containers will be hot and dry due to the heat generated by radioactive decay. However, eventually the temperature will drop to levels where both humid air and aqueous phase corrosion will be possible. As the outer barrier is penetrated, the possibility for crevice formation between the CAM and CRM will exist. Integrated predictive models are being developed to account for the effects of localized environment in the crevice on pit initiation and propagation. For example, a deterministic calculation is used to estimate the accumulation of hydrogen ions (pH suppression) in the crevice due to equilibrium hydrolysis reactions of dissolved iron, nickel and chromium. Sufficient chloride must be transported into the crevice by diffusion and electromigration to satisfy conditions of electroneutrality. Pit initiation and growth within the crevice is dealt with by either a stochastic probability model, or an equivalent deterministic model that is based upon simultaneous integration of the rate expressions for pit embryo formation, the rate of stable pit formation from embryos, and the time-dependent rate of pit propagation.

INNER BARRIER CORROSION

The overall objective of this work is to derive predictive tools that will enable performance assessment of candidate materials during extended periods of time while exposed to Yucca

Mountain conditions. Most recently, attention has been directed towards the development a corrosion model to predict the rate of penetration of the inner barrier, which is comprised of corrosion resistant material (CRM), as a function of the near field environment (NFE). Note that the NFE is characterized by: temperature; humidity; in-drift water dripping; and the chemistry of the contacting water. There are several modes of generalized and localized corrosion that may play an important role in the ultimate failure of engineered barriers used for the geological disposal of high-level radioactive wastes. Penetration of the CRM will be assumed to be due to localized corrosion: pitting and active crevice corrosion. In the case of Alloys 825, 625, C-276, and C-22, all candidates for the CRM, it is evident that a crevice will have to form before significant penetration of the CRM can occur. This model will account for the interaction between the outer barrier, which is comprised of a corrosion allowance material (CAM), and the inner barrier (CRM). Interactions will include: pH suppression in the crevice due to the hydrolysis of products from CAM corrosion; establishment of a mixed potential at the CRM surface; and eventual crevice corrosion of the CRM beneath accumulated corrosion product. Several of these effects will be accounted for with a NFE correction (calculation of pH and mixed potential) applied at the interface between the CAM and CRM, prior to application of the stochastic pitting, or prior to the application of a general corrosion model.

A recent workshop focused on the formulation of model abstractions suitable for application in performance assessment codes. During this workshop, the following hypotheses were formulated: (1) penetration of the outer barrier comprised of CAM will be by either humid air corrosion or aqueous corrosion; (2) the inner barrier comprised of CRM will be exposed in patches as the outer barrier corrodes; (3) the crevice region surrounding each exposed patch can be subdivided into three generic zones. These zones are defined as follows. *Zone 1*: the CRM will be directly exposed to the NFE, via humid air or a thin layer of oxygenated and acidified water. *Zone 2*: the CRM will be exposed to a thin layer of acidified water, with a gradient in oxygen concentration. *Zone 3*: the CRM will be exposed to a thin layer of acidified and deoxygenated water. The corrosion phenomena in these zone may progress through two distinct phases. Furthermore, corrosion within the crevice progresses through two phases. *Phase 1*: active corrosion of the CAM crevice wall. *Phase 2*: classical crevice corrosion of the CRM, with passive-active transition. These zones are illustrated in Figure 1.

During Phase 1, the CAM wall will undergo active anodic dissolution while the CRM wall will be maintained below the damage threshold. The crevice between the CAM and CRM will be filled with water as the temperature of the container drops below 100 °C. This wall will begin to corrode at a rate limited by the availability of cathodic reactants necessary for depolarization of the anodic dissolution reaction. These reactants will probably be dissolved O_2 entering the crevice through the mouth, or H^+ from the electrolyte. The pH of this crevice solution (electrolyte) will be suppressed by various hydrolysis reactions involving dissolved iron. The corrosion potential of the CAM at the point of penetration will be located between the redox potentials for cathodic oxygen reduction (or hydrogen evolution) and anodic iron dissolution. This value can be calculated from mixed potential theory and is expected to be below the damage threshold of the CRM, and is believed to galvanically protect the CRM, though the extent of protection is under debate. Passivation of the crevice wall formed by the CAM will be not be

possible at the pH and potential maintained at the mouth of the crevice. The rate of formation of precipitated products from corrosion of the CAM wall will be greatest near the mouth of the crevice. These hydroxides and oxyhydroxides will accumulate near the crevice mouth, eventually filling the space. During Phase 2, a second crevice will form between the precipitated, tightly packed corrosion products and the CRM. Initially, the two walls of this new crevice will be formed by the precipitated solids, which will be relatively dielectric in nature, and the passive surface of the CRM.

APPROACH

A first-order approach to CAM-CRM interaction will be to account for the effects of CAM corrosion on the localized environment that exists in the crevice separating the outer and inner barriers: suppression of pH due to hydrolysis of corrosion products; initial establishment mixed potential below damage threshold of CRM; and classical crevice corrosion of CRM beneath precipitated corrosion products. These interfacial effects will "set the stage" for localized attack (pitting; active crevice corrosion; etc.) of the CRM, and will be accounted for with an "interfacial NFE correction." This relatively simple correction will facilitate application of other corrosion models at this boundary, including the stochastic pitting model developed by Shibata [1,2], Henshall [3-5], and others.

The interfacial correction of the NFE, which will determine the extent of localized corrosion within the crevice, will be fully developed. The pH in this electrolyte will be suppressed by an accumulation of hydrogen ions from various hydrolysis reactions involving dissolved iron, nickel, chromium, molybdenum and other elements. Here, we begin by accounting for iron, nickel, and chromium. Molybdenum is not yet included. The pH can be calculated by finding values of $[H^+]$ that satisfy a nonlinear mass balance equation. This is equivalent to finding the roots of a polynomial in $[H^+]$. The terms in this equation are defined by: (i) equilibrium constants for hydrolysis and other reactions; (ii) the solubility products for precipitated corrosion products; (iii) the dissociation constant for water; and (iv) total quantity of dissolved metal. Since electroneutrality must be maintained, sufficient Cl⁻ must be transported into the crevice to balance the charge of accumulated hydrogen ions. The corrosion potential of the CAM at the point of penetration will probably be located between the redox potentials for cathodic oxygen reduction and anodic iron dissolution, which can be calculated from mixed potential theory. Furthermore, the CAM corrosion potential (mixed potential) is expected to be below the damage threshold of the CRM, and should galvanically protect the CRM close to the penetration. Passivation of the crevice wall formed by the CAM is not expected at the pH and potential maintained at the mouth of the crevice. The rate of formation of precipitated products from corrosion of the CAM wall will be greatest near the mouth of the crevice. Hydroxides and oxyhydroxides will accumulate near the crevice mouth, eventually filling the space and closing the crevice. These simple concepts will govern the localized environment in Zones 1, 2 and 3, which will set the stage for application of either stochastic or probabilistic models. Necessary data such as equilibrium constants for hydrolysis, oxygen solubility, diffusion coefficients, and electrokinetic rate constants can be gleaned from the literature, and from corrosion experiments now underway at Lawrence Livermore National Laboratory (LLNL).

It is planned to use Shibata's stochastic probability theory [1-2] to predict the nucleation and growth of pits on the CRM during Phase 2. Henshall has recently developed a code, based upon Shibata's probabilistic model, and applied it to candidate barrier materials for the repository [3-5]. It is necessary to enhance these pitting models to account for effects recognized by other investigators. New codes have been used to produce the results shown here. A deterministic crevice model is being developed to define localized conditions with the crevice that lies between the CAM and the CRM. Ultimately, this model will account for: (a) pH suppression due to the hydrolysis of dissolved iron, nickel, and chromium; (b) differential oxygenation in the crevice due to mass transport limitations; (c) the temporal and spatial dependence of general and localized corrosion within the crevice. The pH in Zones 1, 2 and 3 will be determined with equilibrium chemistry models. Thus far, only pH suppression has been dealt with.

PITTING MODELS

Several models have been published for individual modes of corrosion [6]. For example, models for pit initiation include: the halide nuclei theory by Okada [7,8]; the point defect model by Chao, Lin and McDonald [9]; the electrostriction model by Sato [10]; and the stochastic probability model by Shibata [1,2]. Here, a deterministic pitting model that has many of the attributes of Shibata's model will also be introduced for consideration. Models for pit propagation include: the Pickering-Frankenthal model [11], which assumes passive walls and active base; the Galvele modification of the Pickering-Frankenthal model [12], which accounts for the effects of metal ion hydrolysis on pH suppression; and the Beck-Alkire model, which deals with a hemispherical pit covered by a thin, electrically-resistive halide film [13].

Stochastic Pitting Model

The stochastic model developed by this author for pitting of the CRM divides the container surface into a two-dimensional (2D) array of hypothetical cells, where probabilities for the transition from one pitting state to another can be assigned. Nucleation or death of a pit embryo is determined by comparing random numbers, generated by a power residue method, to an environment-dependent birth or death probability, respectively. After a pit embryo reaches a critical age, it is assumed to become a stable pit. This approach has already been explored for modeling pit initiation and growth on high-level waste containers by Henshall [3-5]. However, the Henshall model required additional work to enable it to deal with important environmental parameters, such as pH. This model assumed that the birth and death probabilities were functions of potential, chloride concentration, and temperature alone. More specifically, the effect of pH was not accounted for. Furthermore, it was necessary to assume that the birth probability decayed exponentially with time in order to obtain reasonably shaped pit distributions, number of pits verses depth. Ideally, the birth rate (or birth probability) should be time invariant in such a mechanistic model. Finally, the functions used for calculating the birth and death probabilities could have values much greater than unity ($\gg 1$), though the code limited the values to one (≤ 1). It is better to use probability expressions where all calculated values lie between zero and one, as done by Shibata [2]. This feature has now been incorporated into the stochastic pitting model described here.

Based upon empirical observations regarding the roles of Cl^- and $E - E_{crit}$ on pit initiation (birth), as well as empirical observations regarding the roles of OH^- and $E - E_{pass}$ on repassivation (death), the following equations are assumed for the rates of embryo birth and death:

$$\lambda_1 = \lambda_0 [Cl^-] \exp\left(\frac{\alpha_\lambda F}{RT} (E - E_{crit})\right)$$

$$\mu_1 = \mu_0 [OH^-] \exp\left(-\frac{\alpha_\mu F}{RT} (E - E_{pass})\right)$$

where $[Cl^-]$ is the concentration of the chloride anion; $[OH^-]$ is the concentration of the hydroxyl anion; F is Faraday's constant; R is the universal gas constant; T is the absolute temperature; E is the electrochemical potential applied to the surface; E_{crit} is the critical pitting potential; E_{pass} is the repassivation potential; α_λ and α_μ are constants; and λ_0 and μ_0 are intrinsic rate constants for the birth and death of embryos, respectively. The rate of converting an embryo into a stable pit is referred to as the transition rate, γ_1 . This conversion process is assumed to be thermally activated and governed by the Arrhenius rate law.

$$\gamma_1 = \gamma_0 \exp\left(-\frac{A_\gamma}{RT}\right)$$

where A_γ is the apparent activation energy and γ_0 is the intrinsic rate constant. The induction time, τ_1 , is the age that an embryo must reach before it can become a stable pit. This quantity is also assumed to obey an Arrhenius-like expression.

$$\tau_1 = \tau_0 \exp\left(-\frac{A_\tau}{RT}\right)$$

where A_τ is the apparent activation energy and τ_0 is the intrinsic induction time. As described by Shibata [Eqns. 63 & 64, Ref. 2], the birth probability in a single cell ($0 < \lambda < 1$) is then calculated from the rate as follows.

$$\lambda = 1 - e^{-\lambda_1 \delta t}$$

The death and transition probabilities are calculated in a similar manner.

$$\mu = 1 - e^{-\mu_1 \delta t}$$

$$\gamma = 1 - e^{-\gamma_1 \delta t}$$

At a given time step, an embryo will be born in a vacant cell if the following criteria are met:

$$RND \leq \lambda$$

where RND is a random number. Similarly, an existing embryo will die if:

$$RND \leq \mu$$

An embryo will become a stable pit if both of the following criteria are met:

$$RND \leq \gamma$$

$$\tau_{age} \geq \tau_1$$

where τ_{age} is the age of the embryo under consideration.

Deterministic Pitting Model

A deterministic model has been formulated by the author, and can also be used to predict the transients in vacancy, embryo, and stable pit density. This model gives results comparable to the stochastic pitting model proposed by Shibata, and was motivated by the similarity between adsorption kinetics and the transition probabilities for birth and death presented by Shibata. For example, first consider the kinetic expression for the classic Langmuir adsorption isotherm. The fractional coverage of the surface by the adsorbate, θ_{ads} , and the fractional coverage of the surface by vacancies, θ_{vac} , must sum to one.

$$\theta_{ads} + \theta_{vac} = 1$$

The rate at which sites are covered by adsorbates is:

$$\frac{d\theta_{ads}}{dt} = -k_b\theta_{ads} + k_f C(1 - \theta_{ads})$$

where k_f is the forward (adsorption) rate constant, k_b is the reverse (desorption) rate constant, and C is the liquid or gas phase concentration of the adsorbate. Now consider the equations presented by Shibata [Eqns. 38 & 39, Ref. 2]. The probabilities for existing in either of two states are P_0 and P_1 and must sum to one.

$$P_0 + P_1 = 1$$

The rate at which one transitions from one state to the other is:

$$\frac{dP_0}{dt} = -\lambda_0 P_0 + \mu_1 (1 - P_0)$$

where μ_1 is a forward rate constant and λ_0 is a reverse rate constant. If the probability of finding an embryo is P_0 and the probability of finding a vacancy is $P_1 (1-P_0)$, λ_0 corresponds to the birth probability and μ_1 corresponds to the death probability. In this instance, it should be noted that λ_0 should not be interpreted as the intrinsic rate constant for embryo birth. Now consider the more general case, where cells are filled with vacancies, embryos, or stable pits. The corresponding fractional surface coverages must sum to one.

$$\theta_E + \theta_V + \theta_P = 1$$

where θ_E is the fraction of the surface covered by embryos, θ_V is the fraction of the surface that remains vacant, and θ_P is the fraction of the surface covered by stable pits. The accumulation rate of pit embryos on the surface is determined by the difference in birth and death rates.

$$\frac{d\theta_E}{dt} = k_{birth} [Cl^-]^a (1 - \theta_E - \theta_P) - k_{death} [OH^-]^b \theta_E - k_{pit} \theta_E$$

where k_{birth} is analogous to λ_1 , k_{death} is analogous to μ_1 , and k_{pit} is analogous to γ_1 . Consistent with experience, Cl^- is assumed to promote formation of pit embryos, while OH^- is assumed to promote repassivation and embryo death. It is clear that the proposed model involves competitive adsorption of Cl^- and OH^- . There is no induction time per se. The accumulation rate of stable pits on the surface is then proportional to the fractional coverage of the surface by embryos.

$$\frac{d\theta_P}{dt} = k_{pit} \theta_E$$

This rate expression assumes that a stable pit evolves from a single embryo. In reality, several embryos may coalesce to form a pit. Thus, the dependence of the pit generation rate on θ_E may not be first order. Coalescence of "n" embryos would give rise to an "n-th order" rate expression. These two first order ordinary differential equations can be solved simultaneously by numeric integration with a fourth-order Runge-Kutta algorithm. In some cases, assumptions regarding the relative size of terms in the rate expressions lead to formulation of a useful quasi steady state assumption. For example, assume that the following criteria are met:

$$k_{pit} \theta_E \ll k_{birth} [Cl^-]^a (1 - \theta_E)$$

$$k_{pit} \theta_E \ll k_{death} [OH^-]^b \theta_E$$

Then, the fractional surface coverages by embryos and stable pits can be written as:

$$\theta_E = (1 - \theta_P) \left[\frac{G}{1 + G} \right]$$

$$\theta_p = 1 - \exp\left[-k_{pit} t \frac{G}{1+G}\right]$$

where G is defined in terms of chloride and hydrogen ion concentrations, the dissociation constant for water, and the ratio of birth and death rate constants.

$$G = \frac{k_{birth} [Cl^-]^a [H^+]^b}{k_{death} K_w}$$

Based upon assumed functional forms, which are consistent with empirical observations, the ratio of birth and death rate constants is:

$$\frac{k_{birth}}{k_{death}} = \frac{k_{birth}^o}{k_{death}^o} e^{\frac{nF(E-E_{eq})}{RT}}$$

The growth rate of a stable pit is assumed to be diffusion controlled; it obeys the following relationship.

$$d \approx A\sqrt{t}$$

The author will elaborate on this simple penetration rate law in subsequent publications.

CREVICE CORROSION MODELS

Attention is now directed to corrosion in the crevice separating the CAM and CRM. One of the best known theoretical treatments of crevice corrosion is that published several years ago by France [14,15]. He categorizes crevice corrosion mechanisms based upon the type of concentration cell formed between the mouth and base of the crevice. Specific categories of concentration cells include: metal ion; differential aeration; active-passive; hydrogen ion; neutral salt; and inhibitor. Expressions are presented that enable calculation of the critical depth for crevice corrosion. Similar equations have been published by Gartland [16]. A more mathematically rigorous, numerical model has been developed and published by Oldfield and Sutton [17]. Their model accounts for: depletion of oxygen in the crevice; increased acidity of the crevice solution due to the accumulation of hydrogen ions from hydrolysis reactions involving dissolved metal ions; increased chloride concentration in the crevice, driven by the need to maintain electroneutrality; permanent breakdown of the passive film and active corrosion; and the propagation of crevice corrosion. Unfortunately, the possibility of pit initiation and propagation in the acidified crevice region is not accounted for. Pickering et al. have developed analytical models based upon solution of the one-dimensional Nernst-Planck equation [18-19]. Fluxes of ions are estimated with the Nernst-Planck equation, which governs electromigration, diffusion, and convective transport [20]:

$$\bar{N}_i = -z_i u_i F c_i \bar{\nabla} \Phi - D_i \bar{\nabla} c_i + \bar{v} c_i$$

where N_i is the flux, z_i is the charge, u_i is the mobility, c_i is the concentration and D_i is the diffusivity of the i -th ion; Φ is the potential; and v is the convective velocity of the electrolyte. The current density is then defined in terms of the flux:

$$\bar{i} = -F^2 \bar{\nabla} \Phi \sum_i z_i^2 u_i c_i - F \sum_i z_i D_i \bar{\nabla} c_i$$

Though Pickering et al. assume quasi steady state, it should be noted that transients in concentration can be dealt with through application of the following equation:

$$\frac{\partial c_i}{\partial t} = -\bar{\nabla} \cdot \bar{N}_i + R_i$$

where R_i a homogeneous rate. By assuming one-dimensional (1D) transport, Pickering et al. were able to make the following simplifications:

$$N_{i,x} = -z_i u_i F c_i \frac{d \Phi}{d x} - D_i \frac{d c_i}{d x}$$

$$i_x = -\kappa_x \frac{d \Phi}{d x} - F \sum_i z_i D_i \frac{d c_i}{d x}$$

They also include a term (not shown here) for the passive current density along the crevice walls. The conductance of the crevice solution is estimated from a summation of products formed from the valence, mobility, and concentration of each ion.

$$\kappa_x = -F \sum_i z_i^2 u_i c_i$$

The Pickering-Xu model can be used to calculate potential drop in the crevice, which can then be used to establish criteria for depassivation of the crevice wall. This model provides both potential and current distribution along the length of the crevice. It also enables calculation of a critical depth, d_c , for depassivation. For distances less than the critical depth ($x < d_c$), the crevice walls are assumed to be passive, whereas for distances greater than the critical depth ($x > d_c$), the crevice walls are assumed to be active. More recently, Lillard and Scully have employed linear network theory (equivalent circuit models) for the interpretation of crevice corrosion data [21]. In summary, rigorous modeling of the crevice between the CAM and CRM appears to be possible. However, advances have to be made in order to couple individual mechanistic models (crevice corrosion, pit initiation and growth, and stress corrosion cracking). First, the suppression of pH will be discussed.

Localized Suppression of pH Due to Hydrolysis Reactions

The effects of hydrolysis in the crevice will suppress the pH. In order to account for this effect, it is necessary to account for the net accumulation of hydrogen ions due to the hydrolysis of various dissolved metal ions. The net quantity of hydrogen ions accumulated in the crevice solution is:

$$[H^+] = [H^+]_{Fe(II)} + [H^+]_{Fe(III)} + [H^+]_{Ni(II)} + [H^+]_{Cr(III)} + [H^+]_{Cr(VI)} - [H^+]_{H_2} - [H^+]_{O_2}$$

The dissolution of the CAM generates divalent iron ions that hydrolyze, thereby producing hydrogen ions that accumulate in the crevice. The quantity of hydrogen ions due to such hydrolysis reactions is:

$$[H^+]_{Fe(II)} = 2[Fe(OH)_2](s) + [Fe(OH)^+]$$

The dissolved Fe^{2+} can be converted to Fe^{3+} by: (I) microbial action; (ii) oxidation by naturally occurring MnO_2 or other oxidants; or (ii) anodic oxidation at potentials greater than +0.770 V versus NHE. Once formed, it is assumed that Fe^{3+} can also undergo hydrolysis. The quantity of hydrogen ions produced by such reactions is:

$$[H^+]_{Fe(III)} = 3[Fe(OH)_3](s) + 2[Fe(OH)_2^+] + [Fe(OH)^{2+}]$$

From the discussion in Cotton and Wilkinson [22], it will be assumed that:

$$[Fe(OH)_3](s) \approx 0$$

and that:

$$[Fe(OH)_2^+] \approx 0$$

Therefore,

$$[H^+]_{Fe(III)} \approx [Fe(OH)^{2+}]$$

The precipitated iron hydroxide, $Fe(OH)_2$, can be estimated by deducting the amount of iron contained in various dissolved species from the overall iron accumulation rate in the crevice solution:

$$[Fe(OH)_2](s) = [Fe(II)] - [Fe^{2+}] - [Fe(OH)^+]$$

where $[Fe(II)]$ is the total quantity of dissolved iron in the +2 oxidation state. Ultimately, the CRM will undergo dissolution, thereby producing divalent nickel ions and trivalent chromium ions. The equations for the divalent nickel are analogous to those for the divalent iron:

$$[H^+]_{Ni(II)} = 2[Ni(OH)_2](s) + [Ni(OH)^+]$$

where the precipitated nickel hydroxide is defined by:

$$[Ni(OH)_2](s) = [Ni(II)] - [Ni^{2+}] - [Ni(OH)^+]$$

The equations for the trivalent chromium are analogous to those for the trivalent iron:

$$[H^+]_{Cr(III)} = 3[Cr(OH)_3](s) + 2[Cr(OH)_2^+] + [Cr(OH)^{2+}]$$

where the precipitated chromium hydroxide is defined by:

$$[Cr(OH)_3](s) = [Cr(III)] - [Cr^{3+}] - [Cr(OH)^{2+}] - [Cr(OH)_2^+]$$

The formation of hexavalent chromium from divalent chromium also generates hydrogen ions:

$$[H^+]_{Cr(VI)} = 2[Cr_2O_7^{2-}]$$

The hydrogen ions lost due to cathodic reduction reactions is represented by:

$$[H^+]_{H_2} = 2[H_2]$$

$$[H^+]_{O_2} = 4[O_2]$$

The concentrations of species containing dissolved metal are expressed in terms of the hydrogen ion concentration, as discussed by Oldfield and Sutton [17]. In the case of divalent iron species:

$$[Fe^{2+}] = \frac{K_{3,3}}{[OH^-]^2}; \quad [Fe^{2+}] = \frac{K_{3,3}}{K_w^2} [H^+]^2$$

$$[Fe(OH)^+] = \frac{K_{3,1}[Fe^{2+}]}{[H^+]}; \quad [Fe(OH)^+] = \frac{K_{3,1}K_{3,3}}{K_w^2} [H^+]$$

Here, it is assumed that the concentration of ferric ion is defined in terms of ferrous ion:

$$[Fe^{3+}] \approx [Fe^{2+}] e^{f(E-0.770)}$$

where

$$f = \frac{F}{RT} \approx 38.92 V^{-1}$$

and F is Faraday's constant, R is the universal gas constant, and T is the absolute temperature. The hydrolysis of ferric ion is represented by:

$$[Fe(OH)^{2+}] = \frac{K_{4,1}[Fe^{3+}]}{[H^+]}; \quad [Fe(OH)^{2+}] = \frac{K_{4,1}K_{3,3}}{K_w^2}[H^+] e^{f(E-0.770)}$$

In the case of divalent nickel species:

$$[Ni^{2+}] = \frac{K_{5,3}}{[OH^-]^2}; \quad [Ni^{2+}] = \frac{K_{5,3}}{K_w^2}[H^+]^2$$

$$[Ni(OH)^+] = \frac{K_{5,1}[Ni^{3+}]}{[H^+]}; \quad [Ni(OH)^+] = \frac{K_{5,1}K_{5,3}}{K_w^2}[H^+]$$

In the case of trivalent chromium species:

$$[Cr^{3+}] = \frac{K_{1,3}}{[OH^-]^3}; \quad [Cr^{3+}] = \frac{K_{1,3}}{K_w^3}[H^+]^3$$

$$[Cr(OH)^{2+}] = \frac{K_{1,1}[Cr^{3+}]}{[H^+]}; \quad [Cr(OH)^{2+}] = \frac{K_{1,1}K_{1,3}}{K_w^3}[H^+]^2$$

$$[Cr(OH)_2^+] = \frac{K_{1,2}[Cr(OH)^{2+}]}{[H^+]}; \quad [Cr(OH)_2^+] = \frac{K_{1,1}K_{1,2}K_{1,3}}{K_w^3}[H^+]$$

In the case of hexavalent chromium species, but only if MnO₂ is present:

$$[Cr_2O_7^{2-}] = \frac{K_{2,1}[Cr^{3+}]^2}{[Mn^{2+}]^3[H^+]^2}; \quad [Cr_2O_7^{2-}] = \frac{K_{2,1}K_{1,3}^2[H^+]^4}{K_w^6[Mn^{2+}]^3}$$

Each hydrogen generation term can be replaced, which gives:

$$\begin{aligned} [H^+] = & 2[Fe(II)] + 2[Ni(II)] + 3[Cr(III)] - 4[O_2] - 2[H_2] \\ & - 2[Fe^{2+}] - [Fe(OH)^+] + [Fe(OH)^{2+}] - 2[Ni^{2+}] - [Ni(OH)^+] \\ & - 3[Cr^{2+}] - 2[Cr(OH)^{2+}] - [Cr(OH)_2^+] + 2[Cr_2O_7^{2-}] \end{aligned}$$

Since the individual concentrations are functions of hydrogen ion concentration, $[H^+]$, this equation can also be expressed as a polynomial:

$$a_n[H^+]^n + a_{n-1}[H^+]^{n-1} + a_{n-2}[H^+]^{n-2} + \dots + a_3[H^+]^3 + a_2[H^+]^2 + a_1[H^+] + a_0 = 0$$

where the coefficients are defined in terms of: (i) corrosion rates; (ii) equilibrium constants for hydrolysis reactions; (iii) solubilities of corrosion products; and (iv) the dissociation constant for water. The roots of either equation, which determine the pH, can be easily determined by application of an iterative bisection technique. In the following section, it will be shown how individual concentrations can be rewritten in terms of $[H^+]$. It is necessary to have values for the various hydrolysis equilibrium constants in order to determine the roots of the polynomial, and to determine the extent of pH suppression. Several of these values can be found in the seminal publication on crevice corrosion by Oldfield and Sutton [17]. These values are summarized in Table 1.

Table 1. $K_{i,j}$ for i -th Species and j -th Reaction at 25 °C

Species	i	Ref.	$K_{i,1}$	$K_{i,2}$	$K_{i,3}$	$K_{i,4}$	$K_{i,5}$	$K_{i,5}$
Cr(III)	1	A6,A7	1.58×10^{-4}	6.31×10^{-7}	4.0×10^{-38}	2.00×10^3	3.16×10^4	3.16×10^3
Cr(VI)	2	A7	6.92×10^{-11}					
Fe(II)	3	A6	5.0×10^{-9}		7.9×10^{-16}			
Fe(III)	4	A1	1.84×10^{-3}	unknown	unknown			
Ni(II)	5	A6	3.16×10^{-4}		1.35×10^{-15}			

Iron Chemistry

Electrochemical Reactions. Ferrous ions are formed by the anodic dissolution of either the inner or outer barrier. The dissolution can be assumed to occur via the electrochemical reaction given by Bard and Faulkner [23]:

Ferric ions can then be formed by the electrochemical or biological oxidation of dissolved ferrous ion:

Similar reactions for the overall reaction for the oxidation of ferrous to ferric ion are presented by Cotton and Wilkinson [22]:

The oxidation of Fe^{2+} to Fe^{3+} in neutral solution by molecular oxygen may involve a reaction between $FeOH^{+}$ and $O_2H^{\cdot}$, but the details are uncertain. The ferrous ion can also be oxidized by other common oxidants. The action of NO_3^{-} or NO_2^{-} involves the transient formation of a brown nitrosyl $[FeNO(H_2O)_5]^{2+}$ in the overall reaction [24]:

Solution Equilibria. According to Cotton and Wilkinson [22], aqueous solutions of $Fe(II)$ contain the "pale blue-green" divalent hydroxo ion, $[Fe(H_2O)_6]^{2+}$, in the absence of complexing agents. As discussed by Oldfield and Sutton, it can be assumed that Fe^{2+} undergoes hydrolysis to form $Fe(OH)^{+}$, and $Fe(OH)_2$ [17].

$$K_{3,1} = \frac{[Fe(OH)^{+}][H^{+}]}{[Fe^{2+}]}$$

$$K_{3,3} = [Fe^{2+}][OH^{-}]^2$$

In a similar fashion, one might assume that Fe^{3+} can then undergo hydrolysis to form $Fe(OH)^{2+}$, $Fe(OH)_2^{+}$ and $Fe(OH)_3$.

$$K_{4,1} = \frac{[Fe(OH)^{2+}][H^{+}]}{[Fe^{3+}]}$$

$$K_{4,2} = \frac{[Fe(OH)_3^+][H^+]}{[Fe(OH)^{2+}]}$$

$$K_{4,3} = [Fe^{3+}][OH^-]^3$$

According to Cotton and Wilkinson [22], aqueous solutions of Fe(III) contain the "pale purple" trivalent hydroxo ion, $[Fe(H_2O)_6]^{3+}$. At pH < 1, the sole species present in solution is the aqua ion, Fe^{3+} . However, stepwise hydrolysis occurs at pH > 1. At low concentrations, the main equilibria is believed to be [22]:

For the purpose of this work, $[Fe(OH)(H_2O)_5]^{2+}$ and $[Fe(OH)]^{2+}$ are assumed to be equivalent. A small amount of $[Fe(OH)_2]^{2+}$ may be formed, but the second main species is a diamagnetic μ -oxo dimer:

More condensed species and colloidal gels are formed at pH > 2, which leads to the precipitation of a red-brown gelatinous hydrous oxide. In the presence of complexing ions such as Cl^- , the hydrolysis of Fe^{3+} , or of $FeCl_3$, is more complicated, giving chloro, aqua, and hydroxy species, as well as $[FeCl_4]^-$ at high Cl^- concentrations [25,26].

Nickel Chemistry

Electrochemical Reactions. In alkaline solutions, the anodic dissolution of nickel is believed to occur by the reaction presented by Bard and Faulkner [23]:

This may actually be equivalent to the dissolution of nickel as Ni^{2+} , followed by hydrolysis. In acidic solutions, the dissolution is believed to occur via the electrode reaction presented by Cotton and Wilkinson [22], as well as by Bard and Faulkner [23]:

Solution Equilibria. Nickelous ions are formed by the anodic dissolution of the inner barrier. As discussed by Oldfield and Sutton, the Ni^{2+} then undergoes hydrolysis to form other Ni(II) species, including $Ni(OH)^+$, and $Ni(OH)_2$ [17].

$$K_{s,1} = \frac{[Ni(OH)^+][H^+]}{[Ni^{2+}]}$$

$$K_{s,3} = [Ni^{2+}][OH^-]^2$$

The hydroxide, $Ni(OH)_2$, precipitates from basic aqueous solutions of Ni(II), forming a voluminous green gel that crystallizes with the crystal structure of $Mg(OH)_2$.

Chromium Chemistry

Electrochemical Reactions. Chromium is a white, hard, lustrous, and brittle metal (melting point of 1903 ± 10 °C) [22]. It is extremely resistant to ordinary corrosive agents, which accounts for its extensive use as an electroplated protective coating. The metal dissolves fairly readily in nonoxidizing mineral acids, such as HCl and H_2SO_4 . However, it does not dissolve in concentrated or dilute HNO_3 , or aqua regia. The last two reagents, aqua regia and HNO_3 , passivate the metal in a manner that is not well understood. The electrode potentials of the metal are [22]:

The dissolution could also be assumed to occur via the sequential electrochemical reactions given by Bard and Faulkner [23]:

Solutions of Cr^{2+} are usually produced by reducing Cr^{3+} with Zn, or by cathodic reduction at -0.410 V. In acidic solutions, dichromate anion can be reduced to trivalent chromium cation:

In basic solutions, chromate anion can be reduced to form insoluble chromium hydroxide:

Solution Equilibria. Note that the Cr^{2+} is readily oxidized to Cr^{3+} in the presence of air. Even in the absence of air, the process can be driven by the reduction of water to liberate hydrogen. In aqueous solution, the aqua ion undergoes hydrolysis [27]:

It has been proposed that the oxidation of Cr^{2+} by O_2 first gives CrO_2Cr , which undergoes protonation to $[(\text{H}_2\text{O})_4\text{Cr}(\mu\text{-OH})_2\text{Cr}(\text{H}_2\text{O})_2]^{2+}$; this in turn splits to give the trivalent hydroxo ion, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. The trivalent hydroxo ion can then undergo dimerization with loss of a proton:

A precipitate that consists of H-bonded layers, $[\text{C}(\text{OH})_3(\text{H}_2\text{O})_3]$, is formed with the addition of base. Prior to aging, which takes about one minute, this precipitate readily dissolves in acid. However, aging results in an oligomeric or polymeric structure that is much less soluble [28,29].

As discussed by Cotton and Wilkinson [22], Chromium trioxide (CrO_3) forms a yellow tetrahedral chromate ion (CrO_4^{2-}) at $\text{pH} > 6$; chromate (HCrO_4^-) ion and red-orange dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) at $2 < \text{pH} < 6$; and chromic acid (H_2CrO_4) at $\text{pH} < 1$. The equilibria are as follows:

The base hydrolysis equilibria are:

Cations Ba^{2+} , Pb^{2+} , and Ag^+ react with hexavalent chromium to form insoluble chromates, not dichromates. If any of these cationic species are released from the waste package, the chromate and dichromate will aid in their precipitation. At the present time, barium is being considered as a sintering aid in a ceramic waste form. Furthermore, the species present in solution depend

upon the type of mineral acid used as electrolyte. When hydrochloric acid is used, there is essentially quantitative conversion into the chlorochromate ion; with sulfuric acid a sulfato complex results:

As discussed in Oldfield and Sutton, as well as others, equilibria between Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$, $\text{Cr}(\text{OH})_4^-$, and CrO_2^- [17,30]. This equilibria for the first three species is illustrated by the following equations:

$$K_{1,1} = \frac{[\text{Cr}(\text{OH})^{2+}][\text{H}^+]}{[\text{Cr}^{3+}]}$$

$$K_{1,2} = \frac{[\text{Cr}(\text{OH})_2^+][\text{H}^+]}{[\text{Cr}(\text{OH})^{2+}]}$$

$$K_{1,3} = [\text{Cr}^{3+}][\text{OH}^-]^3$$

It is noteworthy that these species can polymerize [30]. The dimerization reaction is represented by:

with the value of $K_{1,4}$ at 25 °C given as:

$$\log(K_{1,4}) = 3.3$$

Formation of the trimer is represented by:

with the value of $K_{1,5}$ at 25 °C given as:

$$\log(K_{1,5}) = 4.5$$

Finally, formation of the tetramer is represented by:

with the value of $K_{1,6}$ at 25 °C given as:

$$\log(K_{1,6}) = 3.5$$

These polymerization reactions are assumed to be of secondary importance in pH suppression, and are not accounted for in this analysis.

Because of the carcinogenicity and toxicity of Cr(VI) species, numerous studies have recently been conducted on Cr speciation and the kinetics of Cr(III) oxidation to Cr(VI). Fortunately, the only naturally occurring, non-biological oxidants of Cr(III) are manganese oxides [30]. The formation of dichromate, $Cr_2O_7^{2-}$, is shown in the following equation.

$$K_{2,1} = \frac{[Mn^{2+}]^3 [H^+]^2 [Cr_2O_7^{2-}]}{[Cr^{3+}]^2}$$

At 25 °C the value of $K_{2,1}$ is:

$$\log(K_{2,1}) = -10.16$$

In addition to dichromate anion, chromate and hydrochromate may also exist: CrO_4^{2-} and $HCrO_4^-$ [A7].

Water and Oxygen Chemistry

Electrochemical Reactions. The anodic dissolution of chromium, iron, and nickel can be depolarized by the the cathodic reduction of water, which can be represented by one of the following two reactions, depending upon pH [23]:

Anodic dissolution reactions can also be depolarized by hydrogen evolution, which can be represented by one of the following two reactions, depending upon pH [23]:

Solution Equilibria. The dissociation of water is also pH dependent. The concentration of hydroxyl ions can be expressed in terms of the hydrogen ion concentration.

$$K_w = [H^+][OH^-]$$

No Accumulation of Hydrogen Ions and Electroneutrality

In this case, it is assumed that no hydrogen ions accumulate in the crevice solution. These ions are lost during a purge of the acidified crevice solution. This solution is in equilibrium with precipitated corrosion products. The coefficients are determined from the concentrations of ions such as sodium, magnesium, chloride, sulfate, as well as the equilibrium constants for the various hydrolysis reactions, the solubility products of the neutral hydroxides, and K_w . The first step in deriving the polynomial is to write the expression for electroneutrality. The general expression is:

$$\sum_{j=1}^{m_a} n_j^- z_j^- = \sum_{j=1}^{m_c} n_j^+ z_j^+$$

where n_j^- is the molar concentration of the j-th anion, z_j^- is the charge of that anion, m_a is the total number of anionic species, n_j^+ is the molar concentration of the j-th cation, z_j^+ is the charge of that cation, and m_c is the total number of cationic species. This can be written more specifically in terms of anticipated species:

$$\begin{aligned} [OH^-] + [Cl^-] + [F^-] + [NO_3^-] + [HCO_3^-] + 2[SO_4^{2-}] + 2[S^{2-}] + 2[Cr_2O_7^{2-}] = \\ [H^+] + [Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + 2[Mn^{2+}] + 2[Ni^{2+}] + [Ni(OH)^+] + \\ 2[Fe^{2+}] + [Fe(OH)^+] + 3[Fe^{3+}] + 2[Fe(OH)^{2+}] + [Fe(OH)_2^+] + \\ 3[Cr^{3+}] + 2[Cr(OH)^{2+}] + [Cr(OH)_2^+] \end{aligned}$$

Here too the concentrations of dissolved species are expressed in terms of the hydrogen ion concentration, equilibrium constants for the hydrolysis reactions, solubilities of corrosion products, and the dissociation constant for water. In this case, the solution becomes slightly alkaline.

Mass Balance for Dissolution of Metal in the Crevice

The total quantities of dissolved metal are determined by integration of the corrosion rates for the CAM and CRM, respectively. The total quantity of dissolved iron is defined in terms of the integral Fe_T :

$$Fe_T = [Fe(II)] + [Fe(III)]$$

$$Fe_T = Fe_{T,CAM} + Fe_{T,CRM}$$

$$Fe_{T,CAM} = \frac{1}{2F} \left\{ \frac{1}{h_{CAM}} \int_0^{\tau_{CAM}} i_{CAM} dt \right\}$$

$$Fe_{T,CRM} = \frac{1}{2F} \left\{ \frac{\theta_{Fe}(d_c / L)}{h_{CRM}} \int_{\tau_{CAM}}^{\tau_{CRM}} i_{CRM} dt \right\}$$

where $Fe_{T,CAM}$ is the integral for $(0 < t < \tau_{CAM})$; and $Fe_{T,CRM}$ is the integral for $(\tau_{CAM} < t < \tau_{CRM})$; where h_{CAM} is the width of the Phase 1 crevice (separation of the CAM and CRM); h_{CRM} is the width of the Phase 2 crevice (separation of precipitated corrosion product and CAM); τ_{CAM} is the time for active-wall corrosion of CAM in Phase 1 crevice; τ_{CRM} is the time for active corrosion of CRM in Phase 2 crevice ($x \geq d_c$); d_c is the critical distance from Phase 2 crevice required for depassivation; L is the total length of the crevice; θ_{Fe} is the mole fraction of the CRM that is iron; i_{CAM} is the corrosion current of the active CAM wall in the in the Phase 1 crevice; and i_{CRM} is the corrosion current of the depassivated CRM wall. The total quantity of dissolved nickel is defined in terms of the integral Ni_T :

$$Ni_T = [Ni(II)]$$

$$Ni_T = Ni_{T,CAM} + Ni_{T,CRM}$$

$$Ni_{T,CAM} = 0$$

$$Ni_{T,CRM} = \frac{1}{2F} \left\{ \frac{\theta_{Ni}(d_c / L)}{h_{CRM}} \int_{\tau_{CAM}}^{\tau_{CRM}} i_{CRM} dt \right\}$$

The total quantity of dissolved chromium is defined in terms of the integral Cr_T :

$$Cr_T = [Cr(III)] + [Cr(VI)]$$

$$Cr_T = Cr_{T,CAM} + Cr_{T,CRM}$$

$$Cr_{T,CAM} = 0$$

$$Cr_{T,CRM} = \frac{1}{3F} \left\{ \frac{\theta_{Cr}(d_c / L)}{h_{CRM}} \int_0^{\tau_{CAM}} i_{CRM} dt \right\}$$

Mass Balance for Oxygen Reduction and Hydrogen Evolution Reactions

The $[H^+]$ generation term due to oxygen reduction is defined in terms of the integral O_T :

$$O_T = [O_2]$$

$$O_T = O_{T,CAM} + O_{T,CRM}$$

$$O_{T,CAM} = \frac{1}{4F} \left\{ \frac{1}{h_{CAM}} \int_0^{\tau_{CAM}} 4FJ_{O_2,CAM} dt \right\}$$

$$O_{T,CRM} = \frac{1}{4F} \left\{ \frac{(d_c / L)}{h_{CRM}} \int_0^{\tau_{CAM}} 4FJ_{O_2,CRM} dt \right\}$$

where $J_{O_2,CAM}$ is the mass transport-limited oxygen flux into the mouth of a Phase 1 crevice, and $J_{O_2,CRM}$ is the mass-transport limited oxygen flux into the mouth of a Phase 2 crevice. The loss term due to hydrogen evolution is defined in terms of H_T .

$$H_T = [H_2]$$

$$H_T = H_{T,CAM} + H_{T,CRM}$$

$$H_{T,CAM} = \frac{1}{2F} \left\{ \frac{1}{h_{CAM}} \int_0^{\tau_{CAM}} i_{H_2}^o \frac{[H^+]_{I < I^*}}{[H^+]_{ref}} e^{-\frac{EF}{RT}} dt \right\}$$

$$H_{T,CRM} = \frac{1}{2F} \left\{ \frac{(d_c / L)}{h_{CRM}} \int_0^{\tau_{CAM}} i_{H_2}^o \frac{[H^+]_{I < I^*}}{[H^+]_{ref}} e^{-\frac{EF}{RT}} dt \right\}$$

Since the hydrogen ion concentration at ($t < t^*$), and the electrode potential are functions of time, the integral will have to be evaluated numerically. The value of the integral will be used to define the coefficient a_0 , which will be used to calculate the hydrogen ion concentration at ($t = t^*$). It should be noted that the assumption of electroneutrality is implicit in these equations. Therefore, additional anions such as chloride will have to diffuse into the crevice to balance the charge of the hydrogen ions.

It is important to know the relative quantities of Fe(II) and Fe(III), and that those quantities be defined in terms of the integral, Fe_T .

$$[Fe(II)] = \chi Fe_T$$

$$[Fe(III)] = (1 - \chi) Fe_T$$

It is also important to know the relative quantities of Cr(III) and Cr(VI), and that those quantities be defined in terms of the integral, Cr_T .

$$[Cr(III)] = \zeta Cr_T$$

$$[Cr(VI)] = (1 - \zeta) Cr_T$$

The following proportionalities are assumed for polyvalent iron and chromium:

$$\frac{[Fe(II)]}{[Fe(III)]} = \frac{\chi}{1 - \chi}$$

$$\frac{[Fe(II)]}{[Fe(III)]} \approx \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$\frac{[Cr(III)]}{[Cr(VI)]} = \frac{\zeta}{1 - \zeta}$$

$$\frac{[Cr(III)]}{[Cr(VI)]} \approx \frac{[Cr^{3+}]}{[Cr_2O_7^{2-}]}$$

From these ratios, as well as the equations relating soluble iron and chromium species to $[H^+]$, the parameters χ and ζ are found to be:

$$\chi = \frac{1}{1 + e^{f(E-0.770)}}$$

$$\zeta = \frac{K_w [Mn^{2+}]}{K_w [Mn^{2+}] + K_{2,1} K_{1,3} [H^+]}$$

Dissolved iron, nickel, and chromium from the inner barrier are assumed to have the same ratios as in the alloy. The following relationships are assumed:

$$Ni_{T,CRM} = \frac{\theta_{Ni}}{\theta_{Fe}} Fe_{T,CRM} \text{ and } Cr_{T,CRM} = \frac{\theta_{Cr}}{\theta_{Fe}} Fe_{T,CRM}$$

The anodic current associated with the dissolution of the CAM and CRM will be balanced by the cathodic currents associated with reduction of oxygen and hydrogen ion. For a corrosion limited by the availability of depolarizers and ($\tau_{CAM} < t < \tau_{CRM}$), the following relationship should be obeyed:

$$2\theta_{Fe} Fe_{T,CRM} + 2\theta_{Ni} Ni_{T,CRM} + 3\theta_{Cr} Cr_{T,CRM} = 4O_{T,CRM} + 2H_{T,CRM}$$

This can be rewritten as:

$$\left(2 + 2\frac{\theta_{Ni}}{\theta_{Fe}} + 3\frac{\theta_{Cr}}{\theta_{Fe}}\right) Fe_{T,CRM} = 4O_{T,CRM} + 2H_{T,CRM}$$

Therefore:

$$Fe_{T,CRM} = \frac{4O_{T,CRM} + 2H_{T,CRM}}{2 + 2\frac{\theta_{Ni}}{\theta_{Fe}} + 3\frac{\theta_{Cr}}{\theta_{Fe}}}$$

For ($0 < t < \tau_{CAM}$), the terms for nickel and chromium can be eliminated.

$$Fe_{T,CAM} = 2O_{T,CAM} + H_{T,CAM}$$

RESULTS

Stochastic Pitting Model

Figure 2 shows the calculated pit density (number per 100 cm²) as a function of time, based upon the stochastic model. These calculations were performed with arbitrary parametric values to illustrate the general feature of the stochastic pitting model. The source code and parametric values are given in Appendix 1. As expected, the number of vacancies (unpitted area) decreases with time, while the number of stable pits increases. Initially, the number of pit embryos increases rapidly with time. However, the embryo density reaches a maximum and begins to fall

at the point where the rate of embryo conversion to stable pits exceeds the rate of embryo births. The overall pit generation rate is proportional to the embryo density, and also passes through a maximum. Figure 3 shows the corresponding pit distribution, which is typical of those obtained with the stochastic pitting model with time invariant probabilities. Distinguishing characteristics include: peak near the maximum pit depth; and long tail.

Figure 4 shows the calculated pit density (number per 100 cm²) as a function of time, based upon the deterministic kinetic model. These calculations were performed with arbitrary parametric values to illustrate the general feature of this approach. The source code and parametric values are given in Appendix 2. Like the stochastic model, this model also predicts that the number of vacancies (unpitted area) decreases with time, while the number of stable pits increases. Initially, the number of pit embryos increases rapidly with time. However, the embryo density reaches a maximum and begins to fall at the point where the rate of embryo conversion to stable pits exceeds the rate of embryo births. The overall pit generation rate is proportional to the embryo density, and also passes through a maximum. Figure 5 shows the corresponding pit distribution, which is typical of those obtained with the deterministic kinetic pitting model with time invariant probabilities. Like the stochastic model, distinguishing characteristics include: peak near the maximum pit depth; and long tail.

Figure 6 is a prediction of the fractional coverage of the surface by pit embryos as a function of electrode potential, for three arbitrary chloride concentrations (1X, 2X, and 10X). This prediction is based upon the quasi-steady state solution of the governing equations used to formulate the deterministic kinetic pitting model. If one assumes that the cumulative probability of pit initiation is proportional to the fractional coverage of the surface by pit embryos, it is evident that this simple model is capable of predicting the critical pitting potential. For example, one might assume that E_{crit} is the point where θ_E has a value of 0.5 (cumulative probability of 50%). As the potential is increased to levels above E_{crit} , pitting is assured. If the potential is dropped to values below this value, pitting ceases.

Crevice Corrosion Model

The equations for hydrolysis equilibria and the mass balance for hydrogen ions accumulated in the crevice were combined, as discussed in the previous section outlining the crevice corrosion model. Then, a bisection method was used to determine the concentration hydrogen ions that satisfies the combined equations, as a function of dissolved metal accumulated in the crevice. As previously discussed, exact values of hydrolysis equilibrium constants are given in Table 1. In the illustrative example shown in Figure 7, the composition of the metal being dissolved in the crevice is assumed to be Alloy 825, an early CRM candidate material. The accumulation of metal in the crevice was assumed to increase linearly with time (constant crevice corrosion current), and the crevice solution is assumed to be well mixed. The assumption regarding mixing of the solution is not rigorously true, but is used as an approximation to enable the overall effects of pH suppression in the crevice to be accounted for in a tractable manner. As expected, the simple model predicts a rapid drop in pH of the crevice solution as the amount of dissolved metal in the crevice increases. As shown in Figure 8, the concentrations of iron species dissolved in

the crevice solution, which include $[\text{Fe}^{2+}]$, $[\text{Fe}^{3+}]$, $[\text{Fe}(\text{OH})^{2+}]$ and $[\text{Fe}(\text{OH})^+]$, approach asymptotic values. The amount of precipitated ferrous hydroxide per unit volume crevice solution, $[\text{Fe}(\text{OH})_2]$, is also shown. In the cases shown, $[\text{Fe}(\text{OH})_2]$ is insignificant compared to the concentrations of other species. Figures 9 and 10 show comparable calculations for the concentrations of nickel and chromium species dissolved in the crevice solution, respectively. In the case of nickel, $[\text{Ni}^{2+}]$ and $[\text{Ni}(\text{OH})^+]$ are significant, while $[\text{Ni}(\text{OH})_2]$ is insignificant. The concentrations of dissolved chromium species, which include $[\text{Cr}^{3+}]$, $[\text{Cr}(\text{OH})^{2+}]$ and $[\text{Cr}(\text{OH})^{2+}]$ are much lower than the concentrations of dissolved iron and nickel species, which is to be expected. Most of the chromium in equilibrium with the solution will exist as precipitated $[\text{Cr}(\text{OH})_3]$, which helps account for the exceptional passivating properties of the chromium alloying element. In summary, it is important to note that all species dissolved in the crevice solution approach asymptotic values as the amount of dissolved metal increases. Consequently, the pH also approaches an asymptotic value (pH~1). This leads one to a very useful conclusion regarding "model abstractions." When treating localized corrosion within the crevice, one can estimate the asymptotic value of pH and use that value as an input to other corrosion models for predicting rates of localized attack (pitting) of the CRM in the crevice. Clearly, such a simplification would provide great computational advantages for Total System Performance Assessment (TSPA). These calculations were done with the source code shown in Appendix 3.

It is now important to look at the predictions shown in Figures 7 through 10 and determine whether or not those predictions are reasonable. Jones and Wilde have prepared solutions of CrCl_3 , FeCl_2 , and NiCl_2 and measured the pH [31]. Their measurements are summarized in Table 2, as well as in Figure 11. These authors used these valuable data to directly verify the effects of dissolved FeCl_2 , NiCl_2 , and CrCl_3 on pH suppression. The suppression is due to the accumulation of the hydrolysis reactions discussed in previous sections. Clearly, a pH value of approximately 1 is reasonable, as it falls between the values for saturated solutions of FeCl_2 and NiCl_2 . In the case of saturated CrCl_3 solutions, even lower pH values can be reached. This type of pH suppression can exacerbate corrosion of the CRM in the crevice, and lead to enhanced rates of pit initiation and propagation.

Table 2. The pH of Aqueous Solutions of Metal Chloride Salts at Room Temperature

Salt	1 N	1 N	Saturated
FeCl_2	2.1	0.8	0.2
NiCl_2	3.0	2.7	2.7
CrCl_3	1.1	-0.3	-1.4

Integration of Pitting and Crevice Corrosion Models

Figures 12 and 13 illustrate the effect of pH suppression in a hypothetical crevice on CRM pitting, based upon the stochastic pitting model. Figure 12 shows the calculated pit density (number per 100 cm^2) as a function of time for two cases, direct exposure to the near field environment (NFE) and exposure to the low-pH crevice solution. These calculations were performed with arbitrary parametric values to illustrate the general feature of the stochastic

pitting model. The source code and parametric values are given in Appendix 4. As expected, the number of vacancies (unpitted area) decreases with time in both cases, while the number of stable pits increases. Initially, the number of pit embryos increases rapidly with time. However, the embryo density rapidly increases to a maximum and then begins to fall at the point where the rate of embryo conversion to stable pits exceeds the rate of embryo births. The overall pit generation rate is proportional to the embryo density, and also passes through a maximum. Clearly, suppressed pH increases the rate of pit generation, which is consistent with experience. Figure 13 shows the corresponding pit distribution, which is typical of those obtained with the stochastic pitting model with time invariant probabilities. As previously discussed, distinguishing characteristics include: peak near the maximum pit depth; and long tail. Suppressed pH pushes the distribution to greater pit depths, as one would anticipate.

Figures 14 and 15 illustrate the effect of pH suppression in a hypothetical crevice on CRM pitting, based upon the deterministic (kinetic) pitting model. Figure 14 shows the calculated fractional coverage of the surface by pits as a function of time for two cases, direct exposure to the near field environment ($\text{pH} = 6$ and $[\text{Cl}] = 0.005$ arbitrary units) and exposure to the low-pH crevice solution ($\text{pH} = 5$ and $[\text{Cl}] = 0.01$ arbitrary units). These calculations were performed with arbitrary parametric values, given in Table 6, to illustrate the general feature of the deterministic pitting model. As expected, the fractional coverage of the surface by vacancies (unpitted area) decreases with time in both cases, while the fractional coverage of the surface by stable pits increases. Initially, the fractional coverage of the surface by pit embryos increases rapidly with time. However, the coverage by embryos rapidly increases to a maximum and then begins to fall at the point where the rate of embryo conversion to stable pits exceeds the rate of embryo births. The overall pit generation rate is proportional to the embryo coverage, and also passes through a maximum. Clearly, suppressed pH increases the rate of pit generation, which is consistent with experience. Figure 15 shows the corresponding pit distribution, which is similar to those obtained with the stochastic pitting model with time invariant probabilities. As previously discussed, distinguishing characteristics include: peak near the maximum pit depth; and long tail. Suppressed pH pushes the distribution to greater pit depths, as one would anticipate. These calculations were done with the source code in Appendix 5.

Improvements in Stochastic Pitting Models to Enable Realistic Predictions

Another prediction of pit density as a function of time is shown in Figure 16. In this case, the birth probability is assumed to be time dependent and forced to pass through a maximum as time is increased. This is similar to the strategy employed by Henshall. These calculations were performed with parametric values which enabled the stochastic pitting model to mimic the pit distribution observed on Alloy 825 after an exposure of 240 hours [Data of A. Roy, Ref. 5]. Here too the number of vacancies (unpitted area) decreases with time, while the number of stable pits increases. Figure 17 shows the corresponding pit distribution, which is bell shaped, similar to the data of Roy. The source code and parametric values used to generate these predictions is shown in Appendix 6. This distribution and those shown in Figures 13 are compared in Figure 18. Ideally, model parameters such as the birth probability should be time invariant. The rate equations that underlie the stochastic model must be improved so that such empirical fixes do not have to be employed.

Empirical Approach to Crevice Corrosion

Clearly, much more work needs to be done on the mechanistic pitting and crevice corrosion models provided by this report before they can be reliably used to make predictions for TSPA. In the interim period, it is recommended to use empirical rate expressions, based upon experimental data and a general knowledge of such transport-controlled processes:

$$d = d_0 \left(\frac{t}{t_0} \right)^n$$

where d_0 is the penetration depth at time t_0 , d is the penetration depth at time t , and n is the power of the growth law. The compilation of data by Gdowski [32] has been used as the basis of the predictions shown in Figures 19 through 22. In Figure 19, it is assumed that the penetration rate observed in various crevices, or simulated crevice conditions, is linearly proportional to time (penetration proportional to $t^{1/2}$). In this case, penetration of an inner barrier made of either Alloy 625 or C-276 is predicted within 10,000 years, assuming that the wall is 2 cm thick. In this scenario, both materials would fail within the time of interest in the repository. However, if the penetration rate is transport-controlled (penetration proportional to $t^{1/2}$), Alloy C-276 is not penetrated during the 10,000 year period of interest to the repository. In contrast, Alloy 625 also fails in this case. In cases involving dissolved copper-based alloys such as Monel 400, tests with the "Green Death" test solution may be more appropriate since 1% CuCl_2 is present. In this case, there is evidence that Alloy 686 can pass at temperatures below 135°C. Clearly, the exact time dependence of the penetration rate is critical, but unknown. More research is needed to precisely determine the value of the exponent in the empirical rate expression. Based upon this simple empirical model, it appears that Alloys C-276 and C-22 are better choices for fabrication of the EBS inner barrier than Alloys 825 and 625, which are less resistant to crevice corrosion.

SUMMARY

Two independent pitting models have been formulated, one stochastic and the other deterministic. Both are capable of giving comparable qualitative results and predict that vacant surface decreases with time as the number of stable pits increases. The number of pit embryos passes through a maximum as the rate of death and conversion to stable pits exceeds the rate of birth. A rational dependence on chloride concentration, pH, potential and temperature have now been built into both models so that the effects of pH suppression in the crevice can be accounted for. A solid step has now been taken towards integrating a crevice corrosion and pitting model. However, more work is needed.

Ideally, parameters in any kinetic model should be time invariant. In essence, the rate constant for embryos is such a parameter. However, in order to mimic the pit distribution observed on Alloy 825 after an exposure of 240 hours [Data of A. Roy, Ref. 5], it is necessary to assume that the birth rate (and probability) is time dependent, passing through a maximum as time is increased. This is similar to the strategy employed by Henshall. The rate equations that underlie

the stochastic model must be improved so that such empirical fixes do not have to be employed. An improved formulation is under investigation at the present time.

In regard to crevice corrosion, all species dissolved in the crevice solution approach asymptotic values as the amount of dissolved metal increases. Consequently, the pH also approaches an asymptotic value. Clearly, an asymptotic pH value of approximately 1 is reasonable in the case of Alloy 825 since it falls between the values for saturated solutions of FeCl_2 and NiCl_2 . This leads one to a very useful conclusion regarding "model abstractions." When treating localized corrosion within the crevice, one can estimate the asymptotic value of pH and use that value as an input to other corrosion models for predicting rates of localized attack (pitting) of the CRM in the crevice. Clearly, such a simplification would provide great computational advantages for Total System Performance Assessment (TSPA).

Clearly, much more work needs to be done on the mechanistic pitting and crevice corrosion models provided by this report before they can be reliably used to make predictions for TSPA. In the interim period, it is recommended to use empirical rate expressions, based upon experimental data and a general knowledge of such transport-controlled processes. From preliminary predictions based upon published data, it is evident that the exact time dependence of the penetration rate is critical, but unknown. More research is needed to precisely determine the value of the exponent in the empirical rate expression.

ACKNOWLEDGEMENTS

Discussions with D. Stahl, W. Clarke, W. Halsey, D. McCright, G. Henshall, J. Lee, D. Jones, J. Horne, J. Payer and J. Scully were very helpful. This work was done under the auspices of the U.S. Department of Energy (DOE) by Lawrence Livermore National Laboratory (LLNL) under Contract No. W-7405-Eng-48.

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Figure 1a. Definition of Zones in CAM-CRM Crevice

Figure 1b. Definition of Phase 1 in Zone 2

Figure 1c. Definition of Phase 2 in Zone 2

Figure 1d. Definition of Phase 3 in Zone 2

Probabilistic Pitting Model - Transients

Figure 2. PIT999I.FOR - Default Values

Probabilistic Pitting Model - Distribution of Pit Depths

Figure 3. PIT999I.FOR - Default Values

Deterministic Pitting Model - Transients

Figure 4. RK-PIT-B.FOR - Alternative Approaches

Deterministic Pitting Model - Distribution of Pit Depths

Figure 5. RK-PIT-B.FOR - Alternative Approaches

Deterministic Pitting Model - Quasi Steady State Solution

Figure 6. Deterministic Pitting Model - Quasi Steady State - Pitting Potential

Effect of Hydrolysis on Crevice Solution Chemistry

Figure 7. PH-07A.FOR - Assumed Dissolution of Alloy 825

Effect of Hydrolysis on Crevice Solution Chemistry

Figure 8. PH-07A.FOR - Assumed Dissolution of Alloy 825

Effect of Hydrolysis on Crevice Solution Chemistry

Figure 9. PH-07A.FOR - Assumed Dissolution of Alloy 825

Effect of Hydrolysis on Crevice Solution Chemistry

Figure 10. PH-07A.FOR - Assumed Dissolution of Alloy 825

Effect of Hydrolysis on pH of Metal Chloride Solutions

Figure 11. Experimental pH Suppression Data

Modified Stochastic Probability Theory of Pitting

Figure 12. PIT999P.FOR - Effect of pH Suppression in Crevice on Pitting

Modified Stochastic Probability Theory of Pitting

Figure 13. PIT999P.FOR - Effect of pH Suppression in Crevice on Pitting

Application of Heterogeneous Kinetics to Pitting: Effects of Chloride & pH

Figure 14. RK-PIT-C.FOR - Default Values of Adjustable Parameters

Application of Heterogeneous Kinetics to Pitting: Effects of Chloride & pH

Figure 15. RK-PIT-C.FOR - Default Values of Adjustable Parameters

Modified Stochastic Probability Theory of Pitting

Figure 16. PIT999K.FOR - Default Values

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Modified Stochastic Probability Theory of Pitting

Figure 17. PIT999K.FOR - Default Values

Modified Stochastic Probability Theory of Pitting

Figure 8.

OR - Effect of Birth

and Environment

Figure 19. Data Taken from UCRL-ID-108330

Extrapolation ($t^{1.0}$) of Penetration Rates Observed with Alloy 625 and C-276

- Limiting Value Inner Barrier Wall
- Wide Crevice Data (T20) A-625: 5% FeCl₃ & 25C
- Wide Crevice Data (T20) A-625: 5% FeCl₃ + 5% HCl & 25C
- × Wide Crevice Data (T20) A-625: 5% FeCl₃ & 50C
- × Wide Crevice Data (T20) A-625: 5% CuCl₂ & 50C
- Wide Crevice Data (T20) A-625: 5% NaOCl & 50C
- Tight (0.0755 mm) Crevice Data (T20) A-625: 5% FeCl₃ & 50C
- Grooved Block Crevice Data (T22) A-625: 10% FeCl₃ & 25C
- Grooved Block Crevice Data (T22) A-625: 10% FeCl₃ & 50C
- Grooved Block Crevice Data (T22) A-625: 10% FeCl₃ & 75C
- Grooved Block Crevice Data (T22) C-276: 10% FeCl₃ & 25C
- Grooved Block Crevice Data (T22) C-276: 10% FeCl₃ & 50C
- × Grooved Block Crevice Data (T22) C-276: 10% FeCl₃ & 75C
- × General Corrosion (T23) A-625: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 25C
- Pitting Attack (T23) A-625: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 102C
- + General Corrosion (T23) C-276: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 25C
- General Corrosion (T23) C-276: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 102C
- Sea Water - Crevice (T36) A-625: 0.61 m/s SW & 25C
- Brine - General Corrosion (T47) A-625: Holville Brine with 3% TDS & 105C
- ×— Brine - General Corrosion (T47) C-276: Holville Brine with 3% TDS & 105C
- ▲— General, Crevice & Pitting Attack (T50) A-625: Brine A with 306,000 ppm TDS & 250C
- General, Crevice & Pitting Attack (T50) A-625: SW & 250C
- △— General, Crevice & Pitting Attack (T50) C-276: Brine A with 306,000 ppm TDS & 250C
- General, Crevice & Pitting Attack (T50) C-276: SW & 250C

Figure 20. Data Taken from UCRL-ID-108330

Attack of C-276 & A-686 by Green Death ($t^{1/2}$)

- Limiting Value Inner Barrier Wall
- General Corrosion (LLNL T23) C-276: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 102C
- ▲— Crevice Corrosion Data (INCO T14) C-276: Green Death (11.9% H₂SO₄ + 1.3% HCl + 1% FeCl₃ + 1% CuCl₂) & 103C
- Crevice Corrosion Data (INCO T14) A-622: Green Death & 125C
- × Crevice Corrosion Data (INCO T14) A-686: Green Death & 125C
- Crevice Corrosion Data (INCO T14) A-686: Green Death & 135C
- Crevice Corrosion Data (INCO T14) A-686: Green Death & 140C

Figure 21. Data from INCO International

Attack of Alloy 686 & C-276 by Green Death ($t^{1.0}$)

Figure 22. Data from INCO International

Appendix 1. Source Code for Figures 2 and 3

```

PROGRAM PIT999I
C*****
C**** STOCHASTIC PROBABILITY MODEL FOR PITTING BY J.C. FARMER ***
C*****
COMMON/A/TEMP,POT,PH,KW,OH,CL,BIRTH,DEATH,TRANS,GRWTH,DZDT,TAU,DT
REAL*4 TEMP,POT,PH,KW,OH,CL,BIRTH,DEATH,TRANS,GRWTH,DZDT,TAU,DT
COMMON/B/NFLAG,BIRTH0,DEATH0,TRANS0,GRWTH0,TAU0,DZDT0
REAL*4 BIRTH0,DEATH0,TRANS0,GRWTH0,TAU0,DZDT0
COMMON/C/ECORR,ECRIT,EPASS
REAL*4 ECORR,ECRIT,EPASS
REAL*4 RR,SUMRR,TOTRR,AVGRR
REAL*4 TIME
REAL*4 AGE0(100,100),AGE1(100,100),AGE2(100,100),DEPTH(100,100)
REAL*4 RATEV,RATEE,RATES
REAL*4 SUMD,DMIN,DAVG,DMAX,SUM(100),Z(100,100)
INTEGER*4 NV(100,100),NE(100,100),NS(100,100),ND(100,100)
INTEGER*4 NTV0,NTE0,NTS0,NTV,NTE,NTS
C**** OPENING DATA FILE FOR OUTPUT
OPEN(UNIT=1,FILE='DAT999I1.DAT',STATUS='NEW')
OPEN(UNIT=2,FILE='DAT999I2.DAT',STATUS='NEW')
OPEN(UNIT=3,FILE='DAT999I3.DAT',STATUS='NEW')
C**** BANNER OUTPUT TO MONITOR
PRINT *, '*****'
PRINT *, '*** CODE FOR STOCHASTIC PITTING BY J.C.FARMER,LLNL ***'
PRINT *, '*** BASED ON THEORY OF SHIBATA; HENSHAW ARTICLE; ***'
PRINT *, '*** AND MECHANISTIC DEVELOPMENT BY J.C. FARMER ***'
PRINT *, '*** ALL RIGHTS RESERVED - COPYRIGHT - 1997 ***'
PRINT *, '*****'
C**** DEFAULT VALUES OF ENVIRONMENTAL PARAMETERS FOR STOCHASTIC MODEL
TEMP=25
POT=0.8
PH=7.0
CL=35000
C**** DEFAULT VALUES OF ALLOY PARAMETERS FOR STOCHASTIC MODEL
C**** REFERENCE: SS316 TABLE 1 UCID-21362 VOL.3 (SCE SCALE)
ECORR=-0.310
ECRIT=0.250
EPASS=0.030
C**** DEFAULT VALUES OF ADJUSTABLE PARAMETERS
NFLAG=3
BIRTH0=0.1
DEATH0=0.1
TRANS0=0.05
GRWTH0=0.1
DZDT0=1.0E-04
TAU0=5.0
DT=1.0
C**** ACCEPT OR REJECT DEFAULT VALUES OF ADJUSTABLE PARAMETERS
WRITE(*,6000)
6000 FORMAT(2X,'ENTER (999) FOR DEFAULT      =' '\)
READ(*,*)IXXX

```

Appendix 1

```

IF(IXXX.EQ.999)GOTO 9800
7000 CONTINUE
C**** INPUT ENVIRONMENTAL CONDITIONS
WRITE(*,8100)
8100 FORMAT(2X,'TEMPERATURE (DEGREES CENTIGRADE)  =' '\)
READ(*,*)TEMP
WRITE(*,8200)
8200 FORMAT(2X,'PH (DIMENSIONLESS)                =' '\)
READ(*,*)PH
WRITE(*,8300)
8300 FORMAT(2X,'CHLORIDE (PPM)                      =' '\)
READ(*,*)CL
WRITE(*,8400)
8400 FORMAT(2X,'POTENTIAL (VOLTS VS SCE)            =' '\)
READ(*,*)POT
WRITE(*,8500)
8500 FORMAT(2X,'CORROSION POTENTIAL (VOLTS VS SCE) =' '\)
READ(*,*)ECORR
WRITE(*,8600)
8600 FORMAT(2X,'PITTING POTENTIAL (VOLTS VS SCE)   =' '\)
READ(*,*)ECRIT
WRITE(*,8700)
8700 FORMAT(2X,'REPASSIVE POTENTIAL (VOLTS VS SCE) =' '\)
READ(*,*)EPASS
C**** INPUT ADJUSTABLE MODEL PARAMETERS
WRITE(*,9100)
9100 FORMAT(2X,'MODEL (1,2,3)                      =' '\)
READ(*,*)NFLAG
WRITE(*,9200)
9200 FORMAT(2X,'BIRTH0 (EVENTS/TIME OR PROBABILITY) =' '\)
READ(*,*)BIRTH0
WRITE(*,9300)
9300 FORMAT(2X,'DEATH0 (EVENTS/TIME OR PROBABILITY) =' '\)
READ(*,*)DEATH0
WRITE(*,9400)
9400 FORMAT(2X,'TRANS0 (EVENTS/TIME OR PROBABILITY) =' '\)
READ(*,*)TRANS0
WRITE(*,9500)
9500 FORMAT(2X,'GRWTH0 (EVENTS/TIME OR PROBABILITY) =' '\)
READ(*,*)GRWTH0
WRITE(*,9550)
9550 FORMAT(2X,'PENETRATION RATE (DEPTH/TIME)      =' '\)
READ(*,*)DZDT0
WRITE(*,9600)
9600 FORMAT(2X,'TAU0 (TIME)                        =' '\)
READ(*,*)TAU0
WRITE(*,9700)
9700 FORMAT(2X,'DT (TIME)                          =' '\)
READ(*,*)DT
9800 CONTINUE
C**** ECHO INPUT FOR POSSIBLE CORRECTIONS
PRINT *, ' BIRTH0 (EVENTS/TIME OR PROBABILITY) = ',BIRTH0
PRINT *, ' DEATH0 (EVENTS/TIME OR PROBABILITY) = ',DEATH0
PRINT *, ' TRANS0 (EVENTS/TIME OR PROBABILITY) = ',TRANS0

```

Appendix 1

```

PRINT *, GRWTH0 (EVENTS/TIME OR PROBABILITY) = ',GRWTH0
PRINT *, TAU0 (TIME) = ',TAU0
PRINT *, DT (TIME) = ',DT
PRINT *, TEMPERATURE (DEGREES CENTIGRADE) = ',TEMP
PRINT *, PH (DIMENSIONLESS) = ',PH
PRINT *, CHLORIDE (PPM) = ',CL
PRINT *, POTENTIAL (VOLTS VS SCE) = ',POT
PRINT *, CORROSION POTENTIAL (VOLTS VS SCE) = ',ECORR
PRINT *, PITTING POTENTIAL (VOLTS VS SCE) = ',ECRIT
PRINT *, REPASSIVATION POT (VOLTS VS SCE) = ',EPASS
WRITE(*,9900)
9900 FORMAT(2X,'ENTER (999) TO ACCEPT VALUES = '\)
READ(*,*)IXXX
IF(IXXX.NE.999)GOTO 7000
C**** OUTPUT ADJUSTABLE PARAMETERS TO ARCHIEVE FILE
WRITE(1,9950)
WRITE(1,9951)BIRTH0
WRITE(1,9952)DEATH0
WRITE(1,9953)TRANS0
WRITE(1,9954)GRWTH0
WRITE(1,9955)TAU0
WRITE(1,9956)DT
WRITE(1,9957)TEMP
WRITE(1,9958)PH
WRITE(1,9959)CL
WRITE(1,9960)POT
WRITE(1,9961)ECORR
WRITE(1,9962)ECRIT
WRITE(1,9963)EPASS
9950 FORMAT(1X,'AS INPUT *****')
9951 FORMAT(1X,'BIRTH0 (EVENTS/TIME OR PROBABILITY) = ',E12.6)
9952 FORMAT(1X,'DEATH0 (EVENTS/TIME OR PROBABILITY) = ',E12.6)
9953 FORMAT(1X,'TRANS0 (EVENTS/TIME OR PROBABILITY) = ',E12.6)
9954 FORMAT(1X,'GRWTH0 (EVENTS/TIME OR PROBABILITY) = ',E12.6)
9955 FORMAT(1X,'TAU0 (TIME) = ',E12.6)
9956 FORMAT(1X,'DT (TIME) = ',E12.6)
9957 FORMAT(1X,'TEMP (DEGREES CENTIGRADE) = ',E12.6)
9958 FORMAT(1X,'PH (DIMENSIONLESS) = ',E12.6)
9959 FORMAT(1X,'CL (PPM) = ',E12.6)
9960 FORMAT(1X,'POT (VOLTS VS SCE) = ',E12.6)
9961 FORMAT(1X,'ECORR (VOLTS VS SCE) = ',E12.6)
9962 FORMAT(1X,'ECRIT (VOLTS VS SCE) = ',E12.6)
9963 FORMAT(1X,'EPASS (VOLTS VS SCE) = ',E12.6)
C**** CONVERSION OF ENVIRONMENTAL PARAMETER INPUT VALUES
TEMP=TEMP+273.0
CL=CL*(1.0E-03)/(58.44277)
C**** CONVERSION OF PITTING & REPASSIVATION FROM SCE TO NHE
POT=POT-0.2412
ECORR=ECORR-0.2412
ECRIT=ECRIT-0.2412
EPASS=EPASS-0.2412
C**** INITIALIZE RANDOM NUMBER GENERATOR
KK=1
SUMRR=0.0

```

```

TOTRR=0.0
AVGRR=0.0
CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
C**** CALCULATE MAX BIRTH, DEATH, & GROWTH PROBABILITIES
TIME=0.0
C**** CALCULATION OF PITTING PROBABILITIES BASED UPON INPUT
CALL PROBABLE
C**** OUTPUT RESULTS OF INITIAL CALCULATION TO MONITOR & DATA FILE
PRINT *, 'INITIAL TIME (TIME)          =',TIME
PRINT *, 'TEMPERATURE (KELVINS)        =',TEMP
PRINT *, 'PH (DIMENSIONLESS)           =',PH
PRINT *, 'CHLORIDE (MOLES/LITER)        =',CL
PRINT *, 'POTENTIAL (VOLTS VS NHE)      =',POT
PRINT *, 'CORROSION POTENTIAL (VOLTS VS NHE) =',ECORR
PRINT *, 'PITTING POTENTIAL (VOLTS VS NHE) =',ECRIT
PRINT *, 'REPASSIVATION POT (VOLTS VS NHE) =',EPASS
PRINT *, 'BIRTH (EVENTS/TIME OR PROBABILITY) =',BIRTH
PRINT *, 'DEATH (EVENTS/TIME OR PROBABILITY) =',DEATH
PRINT *, 'TRANS (EVENTS/TIME OR PROBABILITY) =',TRANS
PRINT *, 'GRWTH (EVENTS/TIME OR PROBABILITY) =',GRWTH
PRINT *, 'PENETRATION RATE (DEPTH/TIME)   =',DZDT
PRINT *, 'TAU (TIME)                     =',TAU
C**** OUTPUT ADJUSTABLE PARAMETERS TO ARCHIEVE FILE
WRITE(1,1000)
WRITE(1,1001)BIRTH0
WRITE(1,1002)DEATH0
WRITE(1,1003)TRANS0
WRITE(1,1004)GRWTH0
WRITE(1,1005)TAU0
WRITE(1,1006)DT
WRITE(1,1007)TEMP
WRITE(1,1008)PH
WRITE(1,1009)CL
WRITE(1,1010)POT
WRITE(1,1011)ECORR
WRITE(1,1012)ECRIT
WRITE(1,1013)EPASS
1000 FORMAT(1X,'AFTER UNIT CONVERSIONS ***** ')
1001 FORMAT(1X,'BIRTH0 (EVENTS/TIME OR PROBABILITY) =',E12.6)
1002 FORMAT(1X,'DEATH0 (EVENTS/TIME OR PROBABILITY) =',E12.6)
1003 FORMAT(1X,'TRANS0 (EVENTS/TIME OR PROBABILITY) =',E12.6)
1004 FORMAT(1X,'GRWTH0 (EVENTS/TIME OR PROBABILITY) =',E12.6)
1005 FORMAT(1X,'TAU0 (TIME)                      =',E12.6)
1006 FORMAT(1X,'DT (TIME)                        =',E12.6)
1007 FORMAT(1X,'TEMP (KELVINS)                    =',E12.6)
1008 FORMAT(1X,'PH (DIMENSIONLESS)                 =',E12.6)
1009 FORMAT(1X,'CL (MOLES/LITER)                   =',E12.6)
1010 FORMAT(1X,'POT (VOLTS VS NHE)                  =',E12.6)
1011 FORMAT(1X,'ECORR (VOLTS VS NHE)                 =',E12.6)
1012 FORMAT(1X,'ECRIT (VOLTS VS NHE)                 =',E12.6)
1013 FORMAT(1X,'EPASS (VOLTS VS NHE)                 =',E12.6)
C**** INITIALIZE NUMBER OF VACANCIES, EMBRYOS, & STABLE PITS
NTV=NI*NJ
NTE=0

```



```

NTS=0
C**** SPECIFICATION OF NUMBER OF CELLS (AREA)
NI=100
NJ=100
C**** INITIALIZE EMBRYO & SUSTAINED GROWTH COUNT
DO 2 J=1,NJ
DO 1 I=1,NI
NV(I,J)=1
NE(I,J)=0
NS(I,J)=0
ND(I,J)=0
1 DEPTH(I,J)=0.0
2 CONTINUE
C**** WRITE HEADING TO OUTPUT FILE
WRITE(2,2000)
2000 FORMAT(7X,'TIME',1X,'VACANCY',2X,'EMBRYO',4X,'PITS',5X,'PIT RATE')
C**** INITIALIZATION OF TIME
TIME=0.0
C**** SPECIFICATION OF TIME STEPS
NK=150
C**** OUTER LOOP - BEGIN TIME STEPS
DO 300 K=1,NK
C**** INITIALIZE NUMBER OF VACANCIES, EMBRYOS, & STABLE PITS
NTV0=NTV
NTE0=NTE
NTS0=NTS
SUMV=0
SUME=0
SUMS=0
TIME=K*DT
C**** CALCULATE BIRTH, DEATH, & GROWTH PROBABILITIES, ETC.
CALL PROBABLE
C**** SCANNING I-J CELLS FOR EVENTS DURING K-TH TIME STEP
DO 200 J=1,NJ
DO 100 I=1,NI
C**** DETECT STABLE PIT
IF(NS(I,J).EQ.1)GOTO 50
C**** DETECT VACANCY
IF(NV(I,J).EQ.1.AND.NE(I,J).EQ.0)GOTO 60
C**** DETECT EMBRYO
IF(NV(I,J).EQ.0.AND.NE(I,J).EQ.1)GOTO 70
C**** THE PROGRAM SHOULD NOT COME DIRECTLY TO THIS POINT
PRINT *, ' STATE DETECTION ERROR!'
C**** CELL CALCULATIONS FOR DETECTED STABLE PIT
50 CONTINUE
AGE2(I,J)=TIME-AGE1(I,J)
CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
IF(RR.LE.GRWTH.OR.ND(I,J).EQ.1)GOTO 51
GOTO 52
51 CONTINUE
C**** THE STABLE PIT CEASES TO GROW (DEATH OF STABLE PIT)
NV(I,J)=0
NE(I,J)=0
NS(I,J)=1

```

```

ND(I,J)=1
DEPTH(I,J)=DEPTH(I,J)
52 CONTINUE
C**** THE STABLE PIT CONTINUES TO GROW
NV(I,J)=0
NE(I,J)=0
NS(I,J)=1
ND(I,J)=0
DEPTH(I,J)=DEPTH(I,J)+DZDT*DT
GOTO 90
C**** CELL CALCULATIONS FOR DETECTED VACANCY
60 CONTINUE
CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
C**** DETECTION OF EMBRYO BIRTH
IF(RR.LE.BIRTH)GOTO 61
GOTO 90
61 NV(I,J)=0
NE(I,J)=1
NS(I,J)=0
ND(I,J)=0
AGE0(I,J)=TIME
GOTO 90
C**** CELL CALCULATIONS FOR DETECTED EMBRYO
C**** DETECTION OF CRITICAL AGE
70 CONTINUE
AGE=TIME-AGE0(I,J)
CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
IF(RR.LE.TRANS.AND.AGE.GE.TAU)GOTO 71
GOTO 80
71 NV(I,J)=0
NE(I,J)=0
NS(I,J)=1
ND(I,J)=0
AGE1(I,J)=AGE0(I,J)
GOTO 90
C**** CELL CALCULATIONS FOR DETECTED EMBRYO
C**** DETECTION OF EMBRYO DEATH
80 CONTINUE
CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
IF(RR.LE.DEATH)GOTO 72
GOTO 90
72 NV(I,J)=1
NE(I,J)=0
NS(I,J)=0
ND(I,J)=0
C**** DETECTION COMPLETED
90 CONTINUE
C**** EMBRYO & PIT SUMMATION
SUMV=SUMV+NV(I,J)
SUME=SUME+NE(I,J)
SUMS=SUMS+NS(I,J)
100 CONTINUE
200 CONTINUE
C**** END OF I-J CELL SCANNING

```

```

C**** TOTAL EMBRYOS & STABLE PITS COUNTED DURING K-TH TIME STEP
  NTV=SUMV
  NTE=SUME
  NTS=SUMS
C**** CALCULATION OF EMBRYO, DEATH & PITTING RATES
  RATEV=(NTV-NTV0)/(NI*NJ*DT)
  RATEE=(NTE-NTE0)/(NI*NJ*DT)
  RATES=(NTS-NTS0)/(NI*NJ*DT)
C**** OUTPUT RESULTS
  PRINT *,TIME,NTV,NTE,NTS,RATES
  WRITE(2,2001)TIME,NTV,NTE,NTS,RATES
2001 FORMAT(1X,F10.4,3(2X,I6),1X,E12.6)
300 CONTINUE
C**** DETECTION OF THE MINIMUM, MAXIMUM & MEAN PIT DEPTH
  DMAX=0.0
  DMIN=1.0E9
  SUMD=0.0
  SIZE=0.0
  DO 650 J=1,NJ
    DO 650 I=1,NI
      IF(NS(I,J).EQ.0.0)GOTO 650
      IF(DMIN.LE.DEPTH(I,J))GOTO 600
      DMIN=DEPTH(I,J)
      GOTO 620
600 CONTINUE
      IF(DMAX.GE.DEPTH(I,J))GOTO 610
      DMAX=DEPTH(I,J)
      GOTO 620
610 CONTINUE
      SUMD=SUMD+DEPTH(I,J)
620 SIZE=SIZE+1.0
650 CONTINUE
      IF(SIZE.EQ.0.0)GOTO 660
      DAVG=SUMD/SIZE
      GOTO 670
660 PRINT *, ' ERROR IN ESTABLISHING PIT SIZE DISTRIBUTION!'
670 CONTINUE
      PRINT *, ' SIZE=',SIZE
      PRINT *, ' DMIN=',DMIN
      PRINT *, ' DAVG=',DAVG
      PRINT *, ' DMAX=',DMAX
      WRITE(3,3001)SIZE
      WRITE(3,3002)DMIN
      WRITE(3,3003)DAVG
      WRITE(3,3004)DMAX
      WRITE(3,3005)
3001 FORMAT(1X,'SIZE=',E10.4)
3002 FORMAT(1X,'DMIN=',E10.4)
3003 FORMAT(1X,'DAVG=',E10.4)
3004 FORMAT(1X,'DMAX=',E10.4)
3005 FORMAT(1X,'DEPTH(%DMAX)',1X,'PROBABILITY(%')
C**** FORMATION OF THE PROBABILITY DISTRIBUTION FUNCTION FOR PIT DEPTHS
  DO 700 K=1,100
700 SUM(K)=0.0

```

```

DO 710 J=1,NJ
DO 710 I=1,NI
Z(I,J)=DEPTH(I,J)*100.0/DMAX
INDEX=Z(I,J)
SUM(INDEX)=SUM(INDEX)+1
710 CONTINUE
DO 720 K=1,100
SUM(K)=100.0*SUM(K)/SIZE
PRINT *, 'PERCENT OF MAX DEPTH = ',K, 'PROBABILITY = ',SUM(K)
WRITE(3,3006)K,SUM(K)
3006 FORMAT(7X,I4,5X,F10.4)
720 CONTINUE
PRINT *, 'TOTAL RANDOM NUMBERS GENERATED =',TOTRR
PRINT *, 'AVERAGE OF ALL RANDOM NUMBERS =',AVGRR
WRITE(1,1014)
1014 FORMAT(1X,'*****')
WRITE(1,1015)TOTRR
1015 FORMAT(1X,'TOTAL RANDOM NUMBERS GENERATED =',E12.6)
WRITE(1,1016)AVGRR
1016 FORMAT(1X,'AVERAGE OF RANDOM NUMBERS GENERATED =',E12.6)
STOP
END

SUBROUTINE RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
C*****
C*****RANDOM NUMBER ALGORITHM FROM MANUAL OF HP-20S SCIENTIFIC CALC ***
C*****SUBROUTINE WRITTEN BY J.C. FARMER APRIL 6, 1997 *****
C*****
REAL*4 RR,SUMRR,TOTRR,AVGRR
IF(KK.GT.1)GOTO 20
C*****RANDOM NUMBER SEED FOR GENERATOR
RR=0.5284163
20 CONTINUE
C*****RESET COUNTER
C*****COMPUTATION OF RANDOM NUMBER BY ADDITIVE TECHNIQUE
RR=997*RR
JJ=RR
RR=RR-JJ
C*****CALCULATION FO THE AVERAGE OF RANDOM NUMBERS
SUMRR=SUMRR+RR
TOTRR=TOTRR+1.0
AVGRR=SUMRR/TOTRR
KK=KK+1
RETURN
END

SUBROUTINE PROBABLE
C**** CALC OF BIRTH, DEATH, TRANS, & GROWTH PROB; CRITICAL TIME
C**** CALCULATION BY (A) HENSHALL & SHIBATA; (B) FARMER & HENSHALL
COMMON/A/TEMP,POT,PH,KW,OH,CL,BIRTH,DEATH,TRANS,GRWTH,DZDT,TAU,DT
REAL*4 TEMP,POT,PH,KW,OH,CL,BIRTH,DEATH,TRANS,GRWTH,DZDT,TAU,DT
COMMON/B/NFLAG,BIRTH0,DEATH0,TRANS0,GRWTH0,TAU0,DZDT0
REAL*4 BIRTH0,DEATH0,TRANS0,GRWTH0,TAU0,DZDT0
COMMON/C/ECORR,ECRIT,EPASS

```

Appendix 1

```

REAL*4 E CORR, ECRIT, EPASS
IF(NFLAG.EQ.1)GOTO 1
IF(NFLAG.EQ.2)GOTO 2
IF(NFLAG.EQ.3)GOTO 3
C**** CALCULATED RATES AS PER HENSHALL ARTICLE
C**** CONDITIONS FROM TABLE 3 FIGURE 9B OF HENSHALL ARTICLE
1 CONTINUE
RGAS=8.314
A1=6.164E12
A2=4.856
A3=2.7E-4
A4=2.0E-4
B1=0.4
B3=0.4
B4=0.4
B5=0.5
C1=1.0
C2=0.2
C3=0.2
C4=1.1
ACT1=2.27E4
ACT2=1600.
ACT3=750.
ACT4=1.00E4
BIRTH1=A1*(POT-B1)*DEXP(C1*CL)*DEXP(-ACT1/(RGAS*TEMP))
DEATH1=A2*DEXP(-C2*CL)*DEXP(-ACT2/(RGAS*TEMP))
TRANS1=1.0E03
GRWTH1=A4*((POT-B4)**B5)*(CL**C4)*DEXP(ACT4/(RGAS*TEMP))
DZDT1 =DZDT0
TAU1 =A3*DEXP(-B3*POT)*DEXP(-C3*CL)*DEXP(ACT3/(RGAS*TEMP))
C**** FARMER'S CHARGE-TRANSFER MECHANISTIC MODEL FOR RATES
C**** ALSO SEE UCID-21362 VOL. 3 EQN. 7 (OKADA'S MODEL FOR TAU)
2 CONTINUE
RGAS=8.314
KW=1.0E-14
OH=KW/(10.0**(-PH))
D1=0.5
D2=0.5
D3=2.0
EACT1=3.0E4
EACT2=3.0E4
BIRTH1=BIRTH0*(CL**2.0)*DEXP(D1*38.92*(298.0/TEMP)*(POT-ECRIT))
DEATH1=DEATH0*(OH**2.0)*DEXP(D2*38.92*(298.0/TEMP)*(EPASS-POT))
TRANS1=TRANS0*DEXP(-EACT1/(RGAS*TEMP))
GRWTH1=GRWTH0
DZDT1 =DZDT0
TAU1 =TAU0*(CL**4.0)/DEXP(D3*38.92*(298.0/TEMP)*(POT-ECRIT))
100 CONTINUE
C**** CALCULATION OF BOUNDED PROBABILITIES AS PER SHIBATA ET AL.
C**** SEE EQN. 63 OF CORROSION, VOL. 52, NO. 11, PP. 813-830.
BIRTH=1.0-DEXP(-DT*BIRTH1)
DEATH=1.0-DEXP(-DT*DEATH1)
TRANS=1.0-DEXP(-DT*TRANS1)
GRWTH=1.0-DEXP(-DT*GRWTH1)

```

Appendix 1

```

DZDT =DZDT1
TAU =TAU1
GOTO 4
C**** DEFAULT VALUES OF PROBABILITIES
3 CONTINUE
  BIRTH=BIRTH0
  DEATH=DEATH0
  TRANS=TRANS0
  GRWTH=GRWTH0
  DZDT=DZDT0
  TAU=TAU0
4 CONTINUE
  RETURN
  END

```

Input Data for Source Code

```

AS INPUT *****
BIRTH0 (EVENTS/TIME OR PROBABILITY) = .100000E+00
DEATH0 (EVENTS/TIME OR PROBABILITY) = .100000E+00
TRANS0 (EVENTS/TIME OR PROBABILITY) = .500000E-01
GRWTH0 (EVENTS/TIME OR PROBABILITY) = .100000E+00
TAU0 (TIME) = .500000E+01
DT (TIME) = .100000E+01
TEMP (DEGREES CENTIGRADE) = .250000E+02
PH (DIMENSIONLESS) = .700000E+01
CL (PPM) = .350000E+05
POT (VOLTS VS SCE) = .800000E+00
ECORR (VOLTS VS SCE) = -.310000E+00
ECRIT (VOLTS VS SCE) = .250000E+00
EPASS (VOLTS VS SCE) = .300000E-01
AFTER UNIT CONVERSIONS *****
BIRTH0 (EVENTS/TIME OR PROBABILITY) = .100000E+00
DEATH0 (EVENTS/TIME OR PROBABILITY) = .100000E+00
TRANS0 (EVENTS/TIME OR PROBABILITY) = .500000E-01
GRWTH0 (EVENTS/TIME OR PROBABILITY) = .100000E+00
TAU0 (TIME) = .500000E+01
DT (TIME) = .100000E+01
TEMP (KELVINS) = .298000E+03
PH (DIMENSIONLESS) = .700000E+01
CL (MOLES/LITER) = .598877E+00
POT (VOLTS VS NHE) = .558800E+00
ECORR (VOLTS VS NHE) = -.551200E+00
ECRIT (VOLTS VS NHE) = .880000E-02
EPASS (VOLTS VS NHE) = -.211200E+00
*****
TOTAL RANDOM NUMBERS GENERATED = .179458E+07
AVERAGE OF RANDOM NUMBERS GENERATED = .500125E+00

```

Appendix 2. Source Code for Figures 4 and 5

```

PROGRAM RKSPIT$B
C*****
C**** MODEL FOR PITTING BASED ON CHAOS THEORY BY J.C. FARMER ****
C*****
COMMON/A/TEMP,POT,PH,CL,KF,KB,KP,KD
REAL*4 TEMP,POT,PH,CL,KF,KB,KP,KD
REAL*4 TIME,V,E,P
REAL*4 KV1,KV2,KV3,KV4
REAL*4 KE1,KE2,KE3,KE4
REAL*4 KP1,KP2,KP3,KP4
REAL*4 DPDT(1000),DEEP(1000)
C**** OPEN DATA FILE FOR DATA OUTPUT
OPEN(UNIT=1,FILE='RKSPIT$1.DAT',STATUS='NEW')
OPEN(UNIT=2,FILE='RKSPIT$2.DAT',STATUS='NEW')
C**** CALCULATION OF RATE CONSTANTS PRIOR TO INTEGRATION
TEMP=300.0
POT=1.1
PH=5.0
CL=0.01
CALL RATE
PRINT *,KF,KB,KP,KD
C**** INTEGRATION OF RATE EXPRESSION WITH 4TH ORDER RUNGE-KUTTA
DT=10.0
V=1.0
E=0.0
P=0.0
N=1000
DO 1000 I=1,N
KV1=KB*E-KF*CL*V
KE1=KF*CL*V-(KB+KP)*E
KP1=KP*E
KV2=KB*(E+0.5*DT*KE1)-KF*CL*(V+0.5*DT*KV1)
KE2=KF*CL*(V+0.5*DT*KV1)-(KB+KP)*(E+0.5*DT*KE1)
KP2=KP*(E+0.5*DT*KE1)
KV3=KB*(E+0.5*DT*KE2)-KF*CL*(V+0.5*DT*KV2)
KE3=KF*CL*(V+0.5*DT*KV2)-(KB+KP)*(E+0.5*DT*KE2)
KP3=KP*(E+0.5*DT*KE2)
KV4=KB*(E+DT*KE3)-KF*CL*(V+DT*KV3)
KE4=KF*CL*(V+DT*KV3)-(KB+KP)*(E+DT*KE3)
KP4=KP*(E+DT*KE3)
V=V+(DT/6.0)*(KV1+2.0*KV2+2.0*KV3+KV4)
E=E+(DT/6.0)*(KE1+2.0*KE2+2.0*KE3+KE4)
P=P+(DT/6.0)*(KP1+2.0*KP2+2.0*KP3+KP4)
TIME=I*DT
PRINT *,TIME,V,E,P
WRITE(1,500)TIME,V,E,P
500 FORMAT(4(1X,E10.4))
AGE=(N-I+1)*DT
DEEP(N-I+1)=KD*SQRT(AGE)
DPDT(N-I+1)=KP1
1000 CONTINUE

```

Appendix 2

```

DO 2000 I=1,N
PRINT *,DEEP(I),DPDT(I)
WRITE(2,1500)DEEP(I),DPDT(I)
1500 FORMAT(2(1X,E10.4))
2000 CONTINUE
STOP
END

```

SUBROUTINE RATE

C**** CALC OF FORMATION RATES FOR VACANCIES, EMBRYOS, AND STABLE PITS

COMMON/A/TEMP,POT,PH,CL,KF,KB,KP,KD

REAL*4 TEMP,POT,PH,CL,KF,KB,KP,KD

REAL*4 KW,OH,KF0,KB0,KP0,KD0

NFLAG=2

IF(NFLAG.EQ.1)GOTO 1

IF(NFLAG.EQ.2)GOTO 2

IF(NFLAG.EQ.3)GOTO 3

C**** CONDITIONS FROM TABLE 3 FIGURE 9B OF HENSHALL ARTICLE

1 CONTINUE

RGAS=8.314

A1=6.164E12

A2=4.856

A3=2.7E-4

A4=2.0E-4

B1=0.4

B3=0.4

B4=0.4

B5=0.5

C1=1.0

C2=0.2

C3=0.2

C4=1.1

ACT1=2.27E4

ACT2=1600.

ACT3=750.

ACT4=1.00E4

C**** ACTUAL CASE: BIRTH, DEATH, TRANS, & GROWTH RATES; CRIT TIME

C**** AS PER GREG HENSHALL AT LLNL

KF=A1*(POT-B1)*DEXP(C1*CL)*DEXP(-ACT1/(RGAS*TEMP))

KB=A2*DEXP(-C2*CL)*DEXP(-ACT2/(RGAS*TEMP))

KP=1.0/(A3*DEXP(-B3*POT)*DEXP(-C3*CL)*DEXP(ACT3/(RGAS*TEMP)))

KD=A4*((POT-B4)**B5)*(CL**C4)*DEXP(ACT4/(RGAS*TEMP))

GOTO 100

C**** FARMER'S CHARGE-TRANSFER MECHANISTIC MODEL FOR RATES

2 CONTINUE

RGAS=8.314

KW=1.0E-14

OH=KW/(10.0**(-PH))

KF0=1.0E2

KB0=1.0E2

KP0=1.0E2

KD0=1.0E2

ECRIT=1.0

EPASS=0.5

Appendix 2

```
EACT=3.0E4
KF=KF0*(CL**2.0)*DEXP(0.5*38.92*(298.0/TEMP)*(POT-ECRIT))
KB=KB0*(OH**2.0)*DEXP(0.5*38.92*(298.0/TEMP)*(EPASS-POT))
KP=KP0*DEXP(-EACT/(RGAS*TEMP))
KD=KD0*(POT-ECRIT)
GOTO 100
3 CONTINUE
KF=1.0
KB=1.0
KP=1.0
KD=1.0
IF(POT.GE.ECRIT)GOTO 4
KD=0.0
4 CONTINUE
100 CONTINUE
RETURN
END
```

Appendix 3. Source Code for Figures 7 through 10

```

PROGRAM PHTEST7
C**** SOFTWARE BY J.C.FARMER 1996-1997 - COPYRIGHT
C**** DEFINITION OF COMMON BLOCKS
COMMON/PH1/POT,PH,TEMP
COMMON/PH2/ERRPH,ERROR,HCALC,HION,OHION,DO2,O2,DH2,H2
COMMON/PH3/DCR,CR,CRTOT,CR3,CROH12,CROH21,CROH3
COMMON/PH4/DNI,NI,NITOT,NI2,NIOH11,NIOH2
COMMON/PH5/DFE,FE,FETOT,FE2,FE3,FEOH11,FEOH12,FEOH2
COMMON/PH6/K11,K12,K13,K14,K15,K21,K31,K33,K41,K51,K53
COMMON/PH7/X(3),E(3)
C**** SPECIFICATION OF REAL VARIABLES
REAL*4 POT,PH,TEMP
REAL*4 ERRPH,ERROR,HCALC,HION,OHION,O2O,DO2,O2,H2O,DH2,H2
REAL*4 CR0,DCR,CR,CRTOT,CR3,CROH12,CROH21,CROH3
REAL*4 NI0,DNI,NI,NITOT,NI2,NIOH11,NIOH2
REAL*4 FE0,DFE,FE,FETOT,FE2,FE3,FEOH11,FEOH12,FEOH2
REAL*4 K11,K12,K13,K14,K15,K21,K31,K33,K41,K51,K53
REAL*4 X,E
C**** SETUP NEW DATA FILES FOR OUTPUT OF RESULTS
OPEN(UNIT=1,FILE='PH7D1.DAT',STATUS='NEW')
OPEN(UNIT=2,FILE='PH7D2.DAT',STATUS='NEW')
OPEN(UNIT=3,FILE='PH7D3.DAT',STATUS='NEW')
OPEN(UNIT=4,FILE='PH7D4.DAT',STATUS='NEW')
OPEN(UNIT=5,FILE='PH7D5.DAT',STATUS='NEW')
C**** INITIAL CONCENTRATIONS OF CHROMIUM,NICKEL AND IRON
CR=0.0
NI=0.0
FE=0.0
H2=0.0
O2=0.0
C**** INITIALIZATION OF THE TEMPERATURE, POTENTIAL AND PH
TEMP=298
POT=0.770
C**** INPUT VALUES FROM THE KEYBOARD
100 CONTINUE
WRITE(*,200)
200 FORMAT(1X,'INPUT DIFFERENTIAL CR (PPM):' \)
READ(*,*)DCR
WRITE(*,300)
300 FORMAT(1X,'INPUT DIFFERENTIAL NI (PPM):' \)
READ(*,*)DNI
WRITE(*,400)
400 FORMAT(1X,'INPUT DIFFERENTIAL FE (PPM):' \)
READ(*,*)DFE
WRITE(*,500)
500 FORMAT(1X,'INPUT DIFFERENTIAL H2 (PPM):' \)
READ(*,*)DH2
WRITE(*,600)
600 FORMAT(1X,'INPUT DIFFERENTIAL O2 (PPM):' \)
READ(*,*)DO2
WRITE(*,700)

```

Appendix 3

```

700 FORMAT(1X,'INPUT TEMPERATURE (C):' \)
  READ(*,*)TEMP
  WRITE(*,800)
800 FORMAT(1X,'INPUT POTENTIAL (V):' \)
  READ(*,*)POT
C**** ECHO INPUT FOR POSSIBLE CORRECTIONS
  PRINT *, 'DISSOLVED CR (PPM) = ', CR
  PRINT *, 'DISSOLVED NI (PPM) = ', NI
  PRINT *, 'DISSOLVED FE (PPM) = ', FE
  PRINT *, 'DISSOLVED H2 (PPM) = ', H2
  PRINT *, 'DISSOLVED O2 (PPM) = ', O2
  PRINT *, 'TEMPERATURE (C) = ', TEMP
  PRINT *, 'POTENTIAL (V) = ', POT
  WRITE(*,999)
999 FORMAT(1X,'INPUT: (1) FOR CHANGE; (2) FOR CONTINUE:' \)
  READ(*,*)IXXX
  IF(IXXX.EQ.1)GOTO 100
C**** LABELS & FORMAT STATEMENTS FOR EACH DATA OUTPUT FILE
  WRITE(1,8001)
8001 FORMAT(1X,'1,CRTOT,NITOT,FETOT,PH,HCALC,ERROR')
  WRITE(2,8002)
8002 FORMAT(1X,'CR0,CR,CR3,CROH12,CROH21,CROH3')
  WRITE(3,8003)
8003 FORMAT(1X,'NI0,NI,NI2,NIOH11,NIOH2')
  WRITE(4,8004)
8004 FORMAT(1X,'FE0,FE,FE2,FE3,FE0H11,FE0H12,FE0H2')
  WRITE(5,8005)
8005 FORMAT(1X,'1,O2,H2')
C**** BEGIN INCREMENTING THE CONCENTRATIONS
  DO 1000 I=1,100
    CR0=(I-1)*DCR
    NI0=(I-1)*DNI
    FE0=(I-1)*DFE
    O20=(I-1)*DO2
    H20=(I-1)*DH2
C**** CONVERSION OF PPM TO MOLE PER LITER
    CR=CR0*(1.0E-06)*(1000.0)/51.996
    NI=NI0*(1.0E-06)*(1000.0)/58.700
    FE=FE0*(1.0E-06)*(1000.0)/55.847
    O2=O20*(1.0E-06)*(1000.0)/(2.0*15.9994)
    H2=H20*(1.0E-06)*(1000.0)/(2.0*1.0079)
C**** THE SUBROUTINE FOR PH SUPPRESSION IS CALLED
    CALL PHCALC
C**** OUTPUT OF RESULTS FROM CALCULATION
    PRINT *, '*****'
    PRINT *, 'HION HCALC ERROR :', HION, HCALC, ERROR
    PRINT *, 'PH H+ OH- :', PH, HION, OHION
    PRINT *, 'FE2+ FE3+ :', FE2, FE3
    PRINT *, 'NI2+ :', NI2
    PRINT *, 'CR3+ :', CR3
    PRINT *, 'FETOT NITOT CRTOT :', FETOT, NITOT, CRTOT
    PRINT *, 'FE0H2 FE0H11 FE0H12 :', FE0H2, FE0H11, FE0H12
    PRINT *, 'NIOH2 NIOH11 :', NIOH2, NIOH11
    PRINT *, 'CROH3 CROH12 CROH21 :', CROH3, CROH12, CROH21

```

Appendix 3

```

PRINT *, '*****'
WRITE(1,9001)I,CRTOT,NITOT,FETOT,PH,HCALC,ERROR
9001 FORMAT(1X,I4,6(1X,E9.3))
WRITE(2,9002)CR0,CR,CR3,CROH12,CROH21,CROH3
9002 FORMAT(6(1X,E9.3))
WRITE(3,9003)NI0,NI,NI2,NIOH11,NIOH2
9003 FORMAT(5(1X,E9.3))
WRITE(4,9004)FE0,FE,FE2,FE3,FEOH11,FEOH12,FEOH2
9004 FORMAT(7(1X,E9.3))
WRITE(5,9005)I,O2,H2
9005 FORMAT(1X,I4,2(1X,E9.3))
1000 CONTINUE
STOP
END

SUBROUTINE PHCALC
C**** SOFTWARE BY J.C.FARMER 1996-1997 - COPYRIGHT
C**** SUBROUTINE FOR PH SUPPRESSION DUE TO HYDROLYSIS
C**** DEFINITION OF COMMON BLOCKS
COMMON/PH1/POT,PH,TEMP
COMMON/PH2/ERRPH,ERROR,HCALC,HION,OHION,DO2,O2,DH2,H2
COMMON/PH3/DCR,CR,CRTOT,CR3,CROH12,CROH21,CROH3
COMMON/PH4/DNI,NI,NITOT,NI2,NIOH11,NIOH2
COMMON/PH5/DFE,FE,FETOT,FE2,FE3,FEOH11,FEOH12,FEOH2
COMMON/PH6/K11,K12,K13,K14,K15,K21,K31,K33,K41,K51,K53
COMMON/PH7/X(3),E(3)
C**** SPECIFICATION OF REAL VARIABLES
REAL*4 POT,PH,TEMP
REAL*4 ERRPH,ERROR,HCALC,HION,OHION,DO2,O2,DH2,H2
REAL*4 DCR,CR,CRTOT,CR3,CROH12,CROH21,CROH3
REAL*4 DNI,NI,NITOT,NI2,NIOH11,NIOH2
REAL*4 DFE,FE,FETOT,FE2,FE3,FEOH11,FEOH12,FEOH2
REAL*4 K11,K12,K13,K14,K15,K21,K31,K33,K41,K51,K53
REAL*4 X,E
C**** DEFINITION OF EQUILIBRIUM CONSTANTS
K11=1.58E-04
K12=6.31E-07
K13=4.00E-38
K14=2.00E+03
K15=3.16E+04
K21=6.92E-11
K31=5.00E-09
K33=7.90E-16
K41=1.84E-03
K51=3.16E-04
K53=1.35E-15
C**** INITIALIZE THE INITIAL PH VALUES
X(3)=14.0
X(2)=8.0
X(1)=-4.0
C**** ITERATIVE CALCULATION TO DETERMINE PH
PH=14.0
N=1000
DO 2000 I=1,N

```

Appendix 3

C**** BISECTION OF PH RANGE & SELECTION OF SEGMENT WITH MINIMUM ERROR

DO 1000 J=1,3

C**** EQUILIBRIUM CALCULATIONS FOR WATER & OXYGEN

PH=X(J)

HION=10.0**(-PH)

OHION=(1.0E-14)/HION

C**** EQUILIBRIA CALCULATIONS FOR CHROMIUM

IF(CR.EQ.0.0)GOTO 100

CR3=K13/OHION**2.0

CROH12=K11*CR3/HION

CROH21=K12*CROH12/HION

CRTOT=CR3+CROH12+CROH21

CROH3=CR-CRTOT

IF(CROH3.GE.0.0)GOTO 100

CR3=CR/(1.0+K11/HION+K11*K12/HION**2.0)

CROH12=K11*CR3/HION

CROH21=K12*CROH12/HION

CRTOT=CR3+CROH12+CROH21

CROH3=0.0

100 CONTINUE

C**** EQUILIBRIA CALCULATIONS FOR NICKEL

IF(NI.EQ.0.0)GOTO 200

NI2=K53/OHION**2.0

NIOH11=K51*NI2/HION

NITOT=NI2+NIOH11

NIOH2=NI-NITOT

IF(NIOH2.GE.0.0)GOTO 200

NI2=NI/(1.0+K51/HION)

NIOH11=K51*NI2/HION

NITOT=NI2+NIOH11

NIOH2=0.0

200 CONTINUE

IF(FE.EQ.0.0)GOTO 300

FEXX=EXP(38.92*(TEMP/298)*(POT-0.770))

FE2=K33/OHION**2.0

FE3=FE2*FEXX

FEOH11=K31*FE2/HION

FEOH12=K41*FE3/HION

FETOT=FE2+FE3+FEOH11+FEOH12

FEOH2=FE-FETOT

IF(FEOH2.GE.0.0)GOTO 300

FE2=FE/((1.0+K31/HION)+FEXX*(1.0+K41/HION))

FE3=FE2*FEXX

FEOH11=K31*FE2/HION

FEOH12=K41*FE3/HION

FETOT=FE2+FE3+FEOH11+FEOH12

FEOH2=FE-FETOT

IF(FEOH2.GE.0.0)GOTO 300

FEOH2=0.0

300 CONTINUE

HFE=2*FEOH2+FEOH11+FEOH12

HNI=2*NIOH2+NIOH11

HCR=3*CROH3+2*CROH21+CROH12

HO2=4*O2

Appendix 3

```
HH2=2*H2
HCALC=HFE+HNI+HCR-HO2-HH2
ERROR=HION-HCALC
E(J)=ERROR
IF(HION.LE.0.0.OR.HCALC.LE.0.0)GOTO 900
ERRPH=ABS(LOG10(HION)-LOG10(HCALC))
GOTO 950
900 CONTINUE
ERRPH=0.0
950 CONTINUE
C PRINT *,ERRPH
IF(ERRPH.LE.0.01)GOTO 3000
1000 CONTINUE
IF(E(1).LT.0.AND.E(2).LT.0.AND.E(3).GT.0)GOTO 1001
IF(E(1).LT.0.AND.E(2).GT.0.AND.E(3).GT.0)GOTO 1002
IF(E(1).GT.0.AND.E(2).GT.0.AND.E(3).LT.0)GOTO 1003
IF(E(1).GT.0.AND.E(2).LT.0.AND.E(3).LT.0)GOTO 1004
1001 X(3)=X(3)
X(1)=X(2)
C PRINT *, ' FLAG 1'
GOTO 1010
1002 X(3)=X(2)
X(1)=X(1)
C PRINT *, ' FLAG 2'
GOTO 1010
1003 X(3)=X(3)
X(1)=X(2)
C PRINT *, ' FLAG 3'
GOTO 1010
1004 X(3)=X(2)
X(1)=X(1)
C PRINT *, ' FLAG4'
1010 X(2)=(X(1)+X(3))/2.0
2000 CONTINUE
3000 CONTINUE
RETURN
END
```

Appendix 4. Source Code for Figures 12 and 13

```

PROGRAM PIT999P
C*****
C**** STOCHASTIC PROBABILITY MODEL FOR PITTING BY J.C. FARMER ***
C*****
COMMON/A/TEMP,POT,PH,KW,OH,CL,BIRTH,DEATH,TRANS,GRWTH,DZDT,TAU,DT
REAL*4 TEMP,POT,PH,KW,OH,CL,BIRTH,DEATH,TRANS,GRWTH,DZDT,TAU,DT
COMMON/B/NFLAG,BIRTH0,DEATH0,TRANS0,GRWTH0,TAU0,DZDT0
REAL*4 BIRTH0,DEATH0,TRANS0,GRWTH0,TAU0,DZDT0
COMMON/C/ECORR,ECRIT,EPASS
REAL*4 ECORR,ECRIT,EPASS
COMMON/D/TIME,NTV,NTE,NTS
REAL*4 TIME
COMMON/E/ALPHA1,ALPHA2
REAL*4 ALPHA1,ALPHA2
REAL*4 RR,SUMRR,TOTRR,AVGRR
REAL*4 AGE0(100,100),AGE1(100,100),AGE2(100,100),DEPTH(100,100)
REAL*4 RATEV,RATEE,RATES
REAL*4 SUMD,DMIN,DAVG,DMAX,SUM(100),Z(100,100)
INTEGER*4 NV(100,100),NE(100,100),NS(100,100),ND(100,100)
INTEGER*4 NTV0,NTE0,NTS0,NTV,NTE,NTS
C**** OPENING DATA FILE FOR OUTPUT
OPEN(UNIT=1,FILE='DAT999P1.DAT',STATUS='NEW')
OPEN(UNIT=2,FILE='DAT999P2.DAT',STATUS='NEW')
OPEN(UNIT=3,FILE='DAT999P3.DAT',STATUS='NEW')
C**** BANNER OUTPUT TO MONITOR
PRINT *, '*****'
PRINT *, '*** CODE FOR STOCHASTIC PITTING BY J.C.FARMER,LLNL ***'
PRINT *, '*** BASED ON THEORY OF SHIBATA; HENSHAW ARTICLE; ***'
PRINT *, '*** AND MECHANISTIC DEVELOPMENT BY J.C. FARMER ***'
PRINT *, '*** ALL RIGHTS RESERVED - COPYRIGHT - 1997 ***'
PRINT *, '*****'
C**** DEFAULT VALUES OF ENVIRONMENTAL PARAMETERS FOR STOCHASTIC MODEL
C**** REFERENCE: ALLOY 825 TABLE 1 & FIGURE 13 UCID-125300
TEMP=90
POT=0.6432
PH=2.57
CL=50000
C**** DEFAULT VALUES OF ALLOY PARAMETERS FOR STOCHASTIC MODEL
C**** REFERENCE: SS316 TABLE 1 UCID-21362 VOL.3 (SCE SCALE)
ECORR=-0.280
ECRIT=0.230
EPASS=0.0
C**** DEFAULT VALUES OF ADJUSTABLE PARAMETERS
NFLAG=3
BIRTH0=0.30
BIRTH0=0.20
DEATH0=0.20
DEATH0=0.50
TRANS0=0.10
TRANS0=0.05
GRWTH0=0.10

```

Appendix 4

```

DZDT0=3.0E-04
TAU0=1.0
C**** DEFAULT VALUE FOR TIME STEPS
DT=1.0
NK=240
C**** SELECT MODEL (1=HENSHALL; 2=FARMER; 3=FIXED PROBABILITIES)
5000 CONTINUE
WRITE(*,5100)
5100 FORMAT(2X,'MODEL (1,2,3)           =' '\)
READ(*,*)NFLAG
C**** SET TIME STEP FOR SIMULATION
WRITE(*,5200)
5200 FORMAT(2X,'DT (TIME/STEP)         =' '\)
READ(*,*)DT
WRITE(*,5300)
5300 FORMAT(2X,'TIME STEPS             =' '\)
READ(*,*)NK
C**** ECHO MODEL, TIME STEP, AND INCREMENTS FOR POSSIBLE CORRECTION
PRINT *, 'NFLAG (1=HENSHALL;2=FARMER;3=FIXED) =',NFLAG
PRINT *, 'DT (TIME/STEP)                 =' ',DT
PRINT *, 'TIME STEPS                     =' ',NK
WRITE(*,5400)
5400 FORMAT(2X,'ENTER (999) TO ACCEPT VALUES   =' '\)
READ(*,*)IXXX
IF(IXXX.NE.999)GOTO 5000
C**** ACCEPT OR REJECT DEFAULT VALUES OF ADJUSTABLE PARAMETERS
WRITE(*,6000)
6000 FORMAT(2X,'ENTER (999) FOR DEFAULT         =' '\)
READ(*,*)IXXX
IF(IXXX.EQ.999)GOTO 9800
IF(NFLAG.EQ.3)GOTO 9000
C**** INPUT ENVIRONMENTAL CONDITIONS
8000 CONTINUE
WRITE(*,8100)
8100 FORMAT(2X,'TEMPERATURE (DEGREES CENTIGRADE) =' '\)
READ(*,*)TEMP
WRITE(*,8200)
8200 FORMAT(2X,'PH (DIMENSIONLESS)              =' '\)
READ(*,*)PH
WRITE(*,8300)
8300 FORMAT(2X,'CHLORIDE (PPM)                  =' '\)
READ(*,*)CL
WRITE(*,8400)
8400 FORMAT(2X,'POTENTIAL (VOLTS VS SCE)         =' '\)
READ(*,*)POT
WRITE(*,8500)
8500 FORMAT(2X,'CORROSION POTENTIAL (VOLTS VS SCE) =' '\)
READ(*,*)ECORR
WRITE(*,8600)
8600 FORMAT(2X,'PITTING POTENTIAL (VOLTS VS SCE) =' '\)
READ(*,*)ECRIT
WRITE(*,8700)
8700 FORMAT(2X,'REPASSIVE POTENTIAL (VOLTS VS SCE) =' '\)
READ(*,*)EPASS

```


Appendix 4

```

C**** ECHO ENVIRONMENTAL CONDITIONS FOR POSSIBLE CORRECTIONS
PRINT *, TEMPERATURE (DEGREES CENTIGRADE) = ',TEMP
PRINT *, PH (DIMENSIONLESS) = ',PH
PRINT *, CHLORIDE (PPM) = ',CL
PRINT *, POTENTIAL (VOLTS VS SCE) = ',POT
PRINT *, CORROSION POTENTIAL (VOLTS VS SCE) = ',ECORR
PRINT *, PITTING POTENTIAL (VOLTS VS SCE) = ',ECRIT
PRINT *, REPASSIVATION POT (VOLTS VS SCE) = ',EPASS
WRITE(*,8800)
8800 FORMAT(2X,'ENTER (999) TO ACCEPT VALUES = '\)
READ(*,*)IXXX
IF(IXXX.NE.999)GOTO 8000
GOTO 9800
C**** INPUT ADJUSTABLE MODEL PARAMETERS
9000 CONTINUE
WRITE(*,9100)
9100 FORMAT(2X,'PENETRATION RATE (DEPTH/TIME) = '\)
READ(*,*)DZDT0
WRITE(*,9200)
9200 FORMAT(2X,'BIRTH0 (EVENTS/TIME OR PROBABILITY) = '\)
READ(*,*)BIRTH0
WRITE(*,9300)
9300 FORMAT(2X,'DEATH0 (EVENTS/TIME OR PROBABILITY) = '\)
READ(*,*)DEATH0
WRITE(*,9400)
9400 FORMAT(2X,'TRANS0 (EVENTS/TIME OR PROBABILITY) = '\)
READ(*,*)TRANS0
WRITE(*,9500)
9500 FORMAT(2X,'GRWTH0 (EVENTS/TIME OR PROBABILITY) = '\)
READ(*,*)GRWTH0
WRITE(*,9600)
9600 FORMAT(2X,'TAU0 (TIME) = '\)
READ(*,*)TAU0
C**** ECHO ADJUSTABLE PARAMETER INPUT FOR POSSIBLE CORRECTIONS
PRINT *, BIRTH0 (EVENTS/TIME OR PROBABILITY) = ',BIRTH0
PRINT *, DEATH0 (EVENTS/TIME OR PROBABILITY) = ',DEATH0
PRINT *, TRANS0 (EVENTS/TIME OR PROBABILITY) = ',TRANS0
PRINT *, GRWTH0 (EVENTS/TIME OR PROBABILITY) = ',GRWTH0
PRINT *, TAU0 (TIME) = ',TAU0
WRITE(*,9700)
9700 FORMAT(2X,'ENTER (999) TO ACCEPT VALUES = '\)
READ(*,*)IXXX
IF(IXXX.NE.999)GOTO 9000
9800 CONTINUE
C**** OUTPUT ADJUSTABLE PARAMETERS TO ARCHIEVE FILE
WRITE(1,9950)
WRITE(1,9951)BIRTH0
WRITE(1,9952)DEATH0
WRITE(1,9953)TRANS0
WRITE(1,9954)GRWTH0
WRITE(1,9955)TAU0
WRITE(1,9956)DT
WRITE(1,9957)TEMP
WRITE(1,9958)PH

```

Appendix 4

```

WRITE(1,9959)CL
WRITE(1,9960)POT
WRITE(1,9961)ECORR
WRITE(1,9962)ECRIT
WRITE(1,9963)EPASS
9950 FORMAT(1X,'AS INPUT ***** ')
9951 FORMAT(1X,'BIRTH0 (EVENTS/TIME OR PROBABILITY) =',E12.6)
9952 FORMAT(1X,'DEATH0 (EVENTS/TIME OR PROBABILITY) =',E12.6)
9953 FORMAT(1X,'TRANS0 (EVENTS/TIME OR PROBABILITY) =',E12.6)
9954 FORMAT(1X,'GRWTH0 (EVENTS/TIME OR PROBABILITY) =',E12.6)
9955 FORMAT(1X,'TAU0 (TIME) =',E12.6)
9956 FORMAT(1X,'DT (TIME/STEP) =',E12.6)
9957 FORMAT(1X,'TEMP (DEGREES CENTIGRADE) =',E12.6)
9958 FORMAT(1X,'PH (DIMENSIONLESS) =',E12.6)
9959 FORMAT(1X,'CL (PPM) =',E12.6)
9960 FORMAT(1X,'POT (VOLTS VS SCE) =',E12.6)
9961 FORMAT(1X,'ECORR (VOLTS VS SCE) =',E12.6)
9962 FORMAT(1X,'ECRIT (VOLTS VS SCE) =',E12.6)
9963 FORMAT(1X,'EPASS (VOLTS VS SCE) =',E12.6)
C**** CONVERSION OF ENVIRONMENTAL PARAMETER INPUT VALUES
TEMP=TEMP+273.0
CL=CL*(1.0E-03)/(58.44277)
C**** CONVERSION OF PITTING & REPASSIVATION FROM SCE TO NHE
POT=POT-0.2412
ECORR=ECORR-0.2412
ECRIT=ECRIT-0.2412
EPASS=EPASS-0.2412
C**** INITIALIZE RANDOM NUMBER GENERATOR
KK=1
SUMRR=0.0
TOTRR=0.0
AVGRR=0.0
CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
C**** CALCULATE MAX BIRTH, DEATH, & GROWTH PROBABILITIES
C**** CALCULATION OF PITTING PROBABILITIES BASED UPON INPUT
TIME=0.0
CALL PROBABLE
C**** OUTPUT RESULTS OF INITIAL CALCULATION TO MONITOR & DATA FILE
PRINT *, ' INITIAL TIME (TIME) =',TIME
PRINT *, ' TEMPERATURE (KELVINS) =',TEMP
PRINT *, ' PH (DIMENSIONLESS) =',PH
PRINT *, ' CHLORIDE (MOLES/LITER) =',CL
PRINT *, ' POTENTIAL (VOLTS VS NHE) =',POT
PRINT *, ' CORROSION POTENTIAL (VOLTS VS NHE) =',ECORR
PRINT *, ' PITTING POTENTIAL (VOLTS VS NHE) =',ECRIT
PRINT *, ' REPASSIVATION POT (VOLTS VS NHE) =',EPASS
PRINT *, ' BIRTH (EVENTS/TIME OR PROBABILITY) =',BIRTH
PRINT *, ' DEATH (EVENTS/TIME OR PROBABILITY) =',DEATH
PRINT *, ' TRANS (EVENTS/TIME OR PROBABILITY) =',TRANS
PRINT *, ' GRWTH (EVENTS/TIME OR PROBABILITY) =',GRWTH
PRINT *, ' PENETRATION RATE (DEPTH/TIME) =',DZDT
PRINT *, ' TAU (TIME) =',TAU
C**** OUTPUT ADJUSTABLE PARAMETERS TO ARCHIVE FILE
WRITE(1,1000)

```

Appendix 4

```

WRITE(1,1001)BIRTH0
WRITE(1,1002)DEATH0
WRITE(1,1003)TRANS0
WRITE(1,1004)GRWTH0
WRITE(1,1005)TAU0
WRITE(1,1006)DT
WRITE(1,1007)TEMP
WRITE(1,1008)PH
WRITE(1,1009)CL
WRITE(1,1010)POT
WRITE(1,1011)ECORR
WRITE(1,1012)ECRIT
WRITE(1,1013)EPASS
1000 FORMAT(1X,'AFTER UNIT CONVERSIONS ***** ')
1001 FORMAT(1X,'BIRTH0 (EVENTS/TIME OR PROBABILITY) =',E12.6)
1002 FORMAT(1X,'DEATH0 (EVENTS/TIME OR PROBABILITY) =',E12.6)
1003 FORMAT(1X,'TRANS0 (EVENTS/TIME OR PROBABILITY) =',E12.6)
1004 FORMAT(1X,'GRWTH0 (EVENTS/TIME OR PROBABILITY) =',E12.6)
1005 FORMAT(1X,'TAU0 (TIME) =',E12.6)
1006 FORMAT(1X,'DT (TIME) =',E12.6)
1007 FORMAT(1X,'TEMP (KELVINS) =',E12.6)
1008 FORMAT(1X,'PH (DIMENSIONLESS) =',E12.6)
1009 FORMAT(1X,'CL (MOLES/LITER) =',E12.6)
1010 FORMAT(1X,'POT (VOLTS VS NHE) =',E12.6)
1011 FORMAT(1X,'ECORR (VOLTS VS NHE) =',E12.6)
1012 FORMAT(1X,'ECRIT (VOLTS VS NHE) =',E12.6)
1013 FORMAT(1X,'EPASS (VOLTS VS NHE) =',E12.6)
C**** INITIALIZE NUMBER OF VACANCIES, EMBRYOS, & STABLE PITS
      NTV=NI*NJ
      NTE=0
      NTS=0
C**** SPECIFICATION OF NUMBER OF CELLS (AREA)
      NI=100
      NJ=100
C**** INITIALIZE EMBRYO & SUSTAINED GROWTH COUNT
      DO 2 J=1,NJ
      DO 1 I=1,NI
      NV(I,J)=1
      NE(I,J)=0
      NS(I,J)=0
      ND(I,J)=0
      1 DEPTH(I,J)=0.0
      2 CONTINUE
C**** WRITE HEADING TO OUTPUT FILE
      WRITE(2,2000)
      2000 FORMAT(9X,'TIME',1X,'VACANCY',2X,'EMBRYO',4X,'PITS',5X,'PIT RATE')
C**** INITIALIZATION OF TIME
      TIME=0.0
C**** OUTER LOOP - BEGIN TIME STEPS
      DO 300 K=1,NK
C**** INITIALIZE NUMBER OF VACANCIES, EMBRYOS, & STABLE PITS
      NTV0=NTV
      NTE0=NTE
      NTS0=NTS

```

```

SUMV=0
SUME=0
SUMS=0
TIME=K*DT
C**** CALCULATE BIRTH, DEATH, & GROWTH PROBABILITIES, ETC.
CALL PROBABLE
C**** SCANNING I-J CELLS FOR EVENTS DURING K-TH TIME STEP
DO 200 J=1,NJ
DO 100 I=1,NI
C**** DETECT STABLE PIT
IF(NS(I,J).EQ.1)GOTO 50
C**** DETECT VACANCY
IF(NV(I,J).EQ.1.AND.NE(I,J).EQ.0)GOTO 60
C**** DETECT EMBRYO
IF(NV(I,J).EQ.0.AND.NE(I,J).EQ.1)GOTO 70
C**** THE PROGRAM SHOULD NOT COME DIRECTLY TO THIS POINT
PRINT *, 'STATE DETECTION ERROR!'
C**** CELL CALCULATIONS FOR DETECTED STABLE PIT
50 CONTINUE
AGE2(I,J)=TIME-AGE1(I,J)
CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
IF(RR.LE.GRWTH.OR.ND(I,J).EQ.1)GOTO 51
GOTO 52
51 CONTINUE
C**** THE STABLE PIT CEASES TO GROW (DEATH OF STABLE PIT)
NV(I,J)=0
NE(I,J)=0
NS(I,J)=1
ND(I,J)=1
DEPTH(I,J)=DEPTH(I,J)
52 CONTINUE
C**** THE STABLE PIT CONTINUES TO GROW
NV(I,J)=0
NE(I,J)=0
NS(I,J)=1
ND(I,J)=0
IF(DEPTH(I,J).EQ.0.0)GOTO 53
C**** THE GROWTH RATE FOR PIT DEPTH IS A FUNCTION OF DEPTH
DREF=0.05
DEPTH(I,J)=DEPTH(I,J)+DT*DZDT*DREF/DEPTH(I,J)
GOTO 54
53 CONTINUE
DEPTH(I,J)=DEPTH(I,J)+DT*DZDT
54 CONTINUE
GOTO 90
C**** CELL CALCULATIONS FOR DETECTED VACANCY
60 CONTINUE
CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
C**** DETECTION OF EMBRYO BIRTH
IF(RR.LE.BIRTH)GOTO 61
GOTO 90
61 NV(I,J)=0
NE(I,J)=1
NS(I,J)=0

```

Appendix 4

```

ND(I,J)=0
AGE0(I,J)=TIME
GOTO 90
C**** CELL CALCULATIONS FOR DETECTED EMBRYO
C**** DETECTION OF CRITICAL AGE
70 CONTINUE
AGE=TIME-AGE0(I,J)
CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
IF(RR.LE.TRANS.AND.AGE.GE.TAU)GOTO 71
GOTO 80
71 NV(I,J)=0
NE(I,J)=0
NS(I,J)=1
ND(I,J)=0
AGE1(I,J)=AGE0(I,J)
GOTO 90
C**** CELL CALCULATIONS FOR DETECTED EMBRYO
C**** DETECTION OF EMBRYO DEATH
80 CONTINUE
CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
IF(RR.LE.DEATH)GOTO 72
GOTO 90
72 NV(I,J)=1
NE(I,J)=0
NS(I,J)=0
ND(I,J)=0
C**** DETECTION COMPLETED
90 CONTINUE
C**** EMBRYO & PIT SUMMATION
SUMV=SUMV+NV(I,J)
SUME=SUME+NE(I,J)
SUMS=SUMS+NS(I,J)
100 CONTINUE
200 CONTINUE
C**** END OF I-J CELL SCANNING
C**** TOTAL EMBRYOS & STABLE PITS COUNTED DURING K-TH TIME STEP
NTV=SUMV
NTE=SUME
NTS=SUMS
C**** CALCULATION OF EMBRYO, DEATH & PITTING RATES
RATEV=(NTV-NTV0)/(NI*NJ*DT)
RATEE=(NTE-NTE0)/(NI*NJ*DT)
RATES=(NTS-NTS0)/(NI*NJ*DT)
C**** OUTPUT RESULTS
PRINT *,TIME,NTV,NTE,NTS,RATES
WRITE(2,2001)TIME,NTV,NTE,NTS,RATES
2001 FORMAT(1X,E12.6,3(2X,I6),1X,E12.6)
300 CONTINUE
C**** DETECTION OF THE MINIMUM, MAXIMUM & MEAN PIT DEPTH
DMAX=0.0
DMIN=1.0E9
SUMD=0.0
SIZE=0.0
DO 650 J=1,NJ

```

Appendix 4

```

DO 650 I=1,NI
IF(NS(I,J).EQ.0.0)GOTO 650
IF(DMIN.LE.DEPTH(I,J))GOTO 600
DMIN=DEPTH(I,J)
GOTO 620
600 CONTINUE
IF(DMAX.GE.DEPTH(I,J))GOTO 610
DMAX=DEPTH(I,J)
GOTO 620
610 CONTINUE
SUMD=SUMD+DEPTH(I,J)
620 SIZE=SIZE+1.0
650 CONTINUE
IF(SIZE.EQ.0.0)GOTO 660
DAVG=SUMD/SIZE
GOTO 670
660 PRINT *, ' ERROR IN ESTABLISHING PIT SIZE DISTRIBUTION!'
670 CONTINUE
PRINT *, ' SIZE=',SIZE
PRINT *, ' DMIN=',DMIN
PRINT *, ' DAVG=',DAVG
PRINT *, ' DMAX=',DMAX
WRITE(3,3001)SIZE
WRITE(3,3002)DMIN
WRITE(3,3003)DAVG
WRITE(3,3004)DMAX
WRITE(3,3005)
3001 FORMAT(1X,'SIZE=',E10.4)
3002 FORMAT(1X,'DMIN=',E10.4)
3003 FORMAT(1X,'DAVG=',E10.4)
3004 FORMAT(1X,'DMAX=',E10.4)
3005 FORMAT(1X,'DEPTH(%DMAX)',1X,'PROBABILITY(%)' )
C**** FORMATION OF THE PROBABILITY DISTRIBUTION FUNCTION FOR PIT DEPTHS
DO 700 K=1,100
700 SUM(K)=0.0
DO 710 J=1,NJ
DO 710 I=1,NI
Z(I,J)=DEPTH(I,J)*100.0/DMAX
INDEX=Z(I,J)
SUM(INDEX)=SUM(INDEX)+1
710 CONTINUE
DO 720 K=1,100
SUM(K)=100.0*SUM(K)/SIZE
PRINT *, ' PERCENT OF MAX DEPTH = ',K, ' PROBABILITY = ',SUM(K)
WRITE(3,3006)K,SUM(K)
3006 FORMAT(1X,I4,5X,F10.4)
720 CONTINUE
PRINT *, ' TOTAL RANDOM NUMBERS GENERATED =',TOTRR
PRINT *, ' AVERAGE OF ALL RANDOM NUMBERS =',AVGRR
WRITE(1,1014)
1014 FORMAT(1X,'*****' )
WRITE(1,1015)TOTRR
1015 FORMAT(1X,'TOTAL RANDOM NUMBERS GENERATED =',E12.6)
WRITE(1,1016)AVGRR

```

Appendix 4

```
1016 FORMAT(1X,'AVERAGE OF RANDOM NUMBERS GENERATED = ',E12.6)
STOP
END
```

```
SUBROUTINE RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
C*****
C*****RANDOM NUMBER ALGORITHM FROM MANUAL OF HP-20S SCIENTIFIC CALC ***
C*****SUBROUTINE WRITTEN BY J.C. FARMER APRIL 6, 1997 *****
C*****
REAL*4 RR,SUMRR,TOTRR,AVGRR
IF(KK.GT.1)GOTO 20
C*****RANDOM NUMBER SEED FOR GENERATOR
RR=0.5284163
20 CONTINUE
C*****RESET COUNTER
C*****COMPUTATION OF RANDOM NUMBER BY ADDITIVE TECHNIQUE
RR=997*RR
JJ=RR
RR=RR-JJ
C*****CALCULATION FO THE AVERAGE OF RANDOM NUMBERS
SUMRR=SUMRR+RR
TOTRR=TOTRR+1.0
AVGRR=SUMRR/TOTRR
KK=KK+1
RETURN
END
```

```
SUBROUTINE PROBABLE
C**** CALC OF BIRTH, DEATH, TRANS, & GROWTH PROB; CRITICAL TIME
C**** CALCULATION BY (A) HENSHALL & SHIBATA; (B) FARMER & HENSHALL
COMMON/A/TEMP,POT,PH,KW,OH,CL,BIRTH,DEATH,TRANS,GRWTH,DZDT,TAU,DT
REAL*4 TEMP,POT,PH,KW,OH,CL,BIRTH,DEATH,TRANS,GRWTH,DZDT,TAU,DT
COMMON/B/NFLAG,BIRTH0,DEATH0,TRANS0,GRWTH0,TAU0,DZDT0
REAL*4 BIRTH0,DEATH0,TRANS0,GRWTH0,TAU0,DZDT0
COMMON/C/ECORR,ECRIT,EPASS
REAL*4 ECORR,ECRIT,EPASS
COMMON/D/TIME,NTV,NTE,NTS
REAL*4 TIME
COMMON/E/ALPHA1,ALPHA2
REAL*4 ALPHA1,ALPHA2
IF(NFLAG.EQ.1)GOTO 1
IF(NFLAG.EQ.2)GOTO 2
IF(NFLAG.EQ.3)GOTO 3
C**** CALCULATED RATES AS PER HENSHALL ARTICLE
C**** CONDITIONS FROM TABLE 3 FIGURE 9B OF HENSHALL ARTICLE
1 CONTINUE
RGAS=8.314
A1=6.164E12
A2=4.856
A3=2.7E-4
A4=2.0E-4
B1=0.4
B3=0.4
B4=0.4
```

Appendix 4

```

B5=0.5
C1=1.0
C2=0.2
C3=0.2
C4=1.1
ACT1=2.27E4
ACT2=1600.
ACT3=750.
ACT4=1.00E4
BIRTH1=A1*(POT-B1)*DEXP(C1*CL)*DEXP(-ACT1/(RGAS*TEMP))
DEATH1=A2*DEXP(-C2*CL)*DEXP(-ACT2/(RGAS*TEMP))
TRANS1=1.0E03
GRWTH1=A4*((POT-B4)**B5)*(CL**C4)*DEXP(ACT4/(RGAS*TEMP))
DZDT1 =DZDT0
TAU1 =A3*DEXP(-B3*POT)*DEXP(-C3*CL)*DEXP(ACT3/(RGAS*TEMP))
GOTO 100
C**** FARMER'S CHARGE-TRANSFER MECHANISTIC MODEL FOR RATES
C**** ALSO SEE UCID-21362 VOL. 3 EQN. 7 (OKADA'S MODEL FOR TAU)
  2 CONTINUE
  RGAS=8.314
  KW=1.0E-14
  OH=KW/(10.0**(-PH))
  D1=0.5
  D2=0.5
  D3=2.0
  EACT1=3.0E4
  EACT2=3.0E4
  BIRTH0=3.4393E-04
  DEATH0=3.7813E+15
  TRANS0=1.0645E+03
  GRWTH0=1.0536E-01
  DZDT0 =3.0000E-04
  TAU0 =1.0
  BIRTH1=BIRTH0*(CL)*DEXP(D1*38.92*(298.0/TEMP)*(POT-ECRIT))
  DEATH1=DEATH0*(OH)*DEXP(D2*38.92*(298.0/TEMP)*(EPASS-POT))
  TRANS1=TRANS0*DEXP(-EACT1/(RGAS*TEMP))
  GRWTH1=GRWTH0
  DZDT1 =DZDT0
  TAU1 =TAU0
C**** ALPHA1: FRACTIONAL COVERAGE BY VACANCIES
  ALPHA1=(10000.0-NTE-NTS)/10000.0
C**** ALPHA2: FRACTIONAL COVERATE BY EMBRYOS
  ALPHA2=(10000.0-NTV-NTS)/10000.0
C**** ALPHA3: FRACTIONAL COVERAGE BY PITS
  ALPHA3=(10000.0-NTE-NTV)/10000.0
C**** OPTION 1: BIRTH PROBILITY PASSES THROUGH PIT-DEPENDENT MAXIMUM
  BIRTH1=ALPHA1*BIRTH1
C**** CALCULATION OF BOUNDED PROBABILITIES AS PER SHIBATA ET AL.
C**** SEE EQN. 63 OF CORROSION, VOL. 52, NO. 11, PP. 813-830.
  100 CONTINUE
  BIRTH=1.0-DEXP(-DT*BIRTH1)
  DEATH=1.0-DEXP(-DT*DEATH1)
  TRANS=1.0-DEXP(-DT*TRANS1)
  GRWTH=1.0-DEXP(-DT*GRWTH1)

```


Appendix 4

```

DZDT=DZDT1
TAU =TAU1
GOTO 4
C**** DEFAULT VALUES OF PROBABILITIES
3 CONTINUE
  BIRTH=BIRTH0
  DEATH=DEATH0
  TRANS=TRANS0
  GRWTH=GRWTH0
  DZDT=DZDT0
  TAU=TAU0
4 CONTINUE
  RETURN
  END

```

Input Data for Source Code - Case 1

```

AS INPUT *****
BIRTH0 (EVENTS/TIME OR PROBABILITY) = .200000E+00
DEATH0 (EVENTS/TIME OR PROBABILITY) = .500000E+00
TRANS0 (EVENTS/TIME OR PROBABILITY) = .500000E-01
GRWTH0 (EVENTS/TIME OR PROBABILITY) = .100000E+00
TAU0 (TIME) = .100000E+01
DT (TIME/STEP) = .100000E+01
TEMP (DEGREES CENTIGRADE) = .900000E+02
PH (DIMENSIONLESS) = .257000E+01
CL (PPM) = .500000E+05
POT (VOLTS VS SCE) = .643200E+00
ECORR (VOLTS VS SCE) = -.280000E+00
ECRIT (VOLTS VS SCE) = .230000E+00
EPASS (VOLTS VS SCE) = .000000E+00
AFTER UNIT CONVERSIONS *****
BIRTH0 (EVENTS/TIME OR PROBABILITY) = .343930E-03
DEATH0 (EVENTS/TIME OR PROBABILITY) = .378130E+16
TRANS0 (EVENTS/TIME OR PROBABILITY) = .106450E+04
GRWTH0 (EVENTS/TIME OR PROBABILITY) = .105360E+00
TAU0 (TIME) = .100000E+01
DT (TIME) = .100000E+01
TEMP (KELVINS) = .363000E+03
PH (DIMENSIONLESS) = .257000E+01
CL (MOLES/LITER) = .855538E+00
POT (VOLTS VS NHE) = .402000E+00
ECORR (VOLTS VS NHE) = -.521200E+00
ECRIT (VOLTS VS NHE) = -.112000E-01
EPASS (VOLTS VS NHE) = -.241200E+00
*****
TOTAL RANDOM NUMBERS GENERATED = .255494E+07
AVERAGE OF RANDOM NUMBERS GENERATED = .500088E+00

```

Input Data for Source Code - Case 2

AS INPUT *****

BIRTH0 (EVENTS/TIME OR PROBABILITY) = .200000E+00
 DEATH0 (EVENTS/TIME OR PROBABILITY) = .500000E+00
 TRANS0 (EVENTS/TIME OR PROBABILITY) = .500000E-01
 GRWTH0 (EVENTS/TIME OR PROBABILITY) = .100000E+00
 TAU0 (TIME) = .100000E+01
 DT (TIME/STEP) = .100000E+01
 TEMP (DEGREES CENTIGRADE) = .900000E+02
 PH (DIMENSIONLESS) = .600000E+01
 CL (PPM) = .500000E+04
 POT (VOLTS VS SCE) = .643200E+00
 ECORR (VOLTS VS SCE) = -.280000E+00
 ECRIT (VOLTS VS SCE) = .230000E+00
 EPASS (VOLTS VS SCE) = .000000E+00

AFTER UNIT CONVERSIONS *****

BIRTH0 (EVENTS/TIME OR PROBABILITY) = .343930E-03
 DEATH0 (EVENTS/TIME OR PROBABILITY) = .378130E+16
 TRANS0 (EVENTS/TIME OR PROBABILITY) = .106450E+04
 GRWTH0 (EVENTS/TIME OR PROBABILITY) = .105360E+00
 TAU0 (TIME) = .100000E+01
 DT (TIME) = .100000E+01
 TEMP (KELVINS) = .363000E+03
 PH (DIMENSIONLESS) = .600000E+01
 CL (MOLES/LITER) = .855538E-01
 POT (VOLTS VS NHE) = .402000E+00
 ECORR (VOLTS VS NHE) = -.521200E+00
 ECRIT (VOLTS VS NHE) = -.112000E-01
 EPASS (VOLTS VS NHE) = -.241200E+00

*****

TOTAL RANDOM NUMBERS GENERATED = .243469E+07
 AVERAGE OF RANDOM NUMBERS GENERATED = .500092E+00

Appendix 5. Source Code for Figures 14 and 15

```

PROGRAM RKSPITSC
C*****
C**** MODEL FOR PITTING BASED ON CHAOS THEORY BY J.C. FARMER ****
C*****
COMMON/A/TEMP,POT,PH,CL,KF,KB,KP,KD
REAL*4 TEMP,POT,PH,CL,KF,KB,KP,KD
REAL*4 TIME,V,E,P
REAL*4 KV1,KV2,KV3,KV4
REAL*4 KE1,KE2,KE3,KE4
REAL*4 KP1,KP2,KP3,KP4
REAL*4 DELPIT(1000),DEEP(1000)
C**** OPEN DATA FILE FOR DATA OUTPUT
OPEN(UNIT=1,FILE='RKPITSC1.DAT',STATUS='NEW')
OPEN(UNIT=2,FILE='RKPITSC2.DAT',STATUS='NEW')
C**** CALCULATION OF RATE CONSTANTS PRIOR TO INTEGRATION
TEMP=300.0
POT=1.1
PH=5.0
CL=0.01
PH=6.0
CL=0.005
CALL RATE
PRINT *,KF,KB,KP,KD
C**** INTEGRATION OF RATE EXPRESSION WITH 4TH ORDER RUNGE-KUTTA
DT=10.0
V=1.0
E=0.0
P=0.0
N=1000
DO 1000 I=1,N
KV1=KB*E-KF*CL*V
KE1=KF*CL*V-(KB+KP)*E
KP1=KP*E
KV2=KB*(E+0.5*DT*KE1)-KF*CL*(V+0.5*DT*KV1)
KE2=KF*CL*(V+0.5*DT*KV1)-(KB+KP)*(E+0.5*DT*KE1)
KP2=KP*(E+0.5*DT*KE1)
KV3=KB*(E+0.5*DT*KE2)-KF*CL*(V+0.5*DT*KV2)
KE3=KF*CL*(V+0.5*DT*KV2)-(KB+KP)*(E+0.5*DT*KE2)
KP3=KP*(E+0.5*DT*KE2)
KV4=KB*(E+DT*KE3)-KF*CL*(V+DT*KV3)
KE4=KF*CL*(V+DT*KV3)-(KB+KP)*(E+DT*KE3)
KP4=KP*(E+DT*KE3)
V=V+(DT/6.0)*(KV1+2.0*KV2+2.0*KV3+KV4)
E=E+(DT/6.0)*(KE1+2.0*KE2+2.0*KE3+KE4)
P=P+(DT/6.0)*(KP1+2.0*KP2+2.0*KP3+KP4)
TIME=I*DT
PRINT *,TIME,V,E,P
WRITE(1,500)TIME,V,E,P
500 FORMAT(4(1X,E10.4))
AGE=(N-I+1)*DT
DEEP(N-I+1)=KD*SQRT(AGE)

```

Appendix 5

```

      DELPIT(N-I+1)=(DT/6.0)*(KP1+2.0*KP2+2.0*KP3+KP4)
1000 CONTINUE
      DO 2000 I=1,N
      PRINT *,DEEP(I),DELPIT(I)
      WRITE(2,1500)DEEP(I),DELPIT(I)
1500 FORMAT(2(1X,E10.4))
2000 CONTINUE
      STOP
      END

```

SUBROUTINE RATE

C**** CALC OF FORMATION RATES FOR VACANCIES, EMBRYOS, AND STABLE PITS

```

      COMMON/A/TEMP,POT,PH,CL,KF,KB,KP,KD
      REAL*4 TEMP,POT,PH,CL,KF,KB,KP,KD
      REAL*4 KW,OH,KF0,KB0,KP0,KD0
      NFLAG=2
      IF(NFLAG.EQ.1)GOTO 1
      IF(NFLAG.EQ.2)GOTO 2
      IF(NFLAG.EQ.3)GOTO 3

```

C**** CONDITIONS FROM TABLE 3 FIGURE 9B OF HENSHALL ARTICLE

```

1 CONTINUE
  RGAS=8.314
  A1=6.164E12
  A2=4.856
  A3=2.7E-4
  A4=2.0E-4
  B1=0.4
  B3=0.4
  B4=0.4
  B5=0.5
  C1=1.0
  C2=0.2
  C3=0.2
  C4=1.1
  ACT1=2.27E4
  ACT2=1600.
  ACT3=750.
  ACT4=1.00E4

```

C**** ACTUAL CASE: BIRTH, DEATH, TRANS, & GROWTH RATES; CRIT TIME

C**** AS PER GREG HENSHALL AT LLNL

```

  KF=A1*(POT-B1)*DEXP(C1*CL)*DEXP(-ACT1/(RGAS*TEMP))
  KB=A2*DEXP(-C2*CL)*DEXP(-ACT2/(RGAS*TEMP))
  KP=1.0/(A3*DEXP(-B3*POT)*DEXP(-C3*CL)*DEXP(ACT3/(RGAS*TEMP)))
  KD=A4*((POT-B4)**B5)*(CL**C4)*DEXP(ACT4/(RGAS*TEMP))
  GOTO 100

```

C**** FARMER'S CHARGE-TRANSFER MECHANISTIC MODEL FOR RATES

```

2 CONTINUE
  RGAS=8.314
  KW=1.0E-14
  OH=KW/(10.0**(-PH))
  KF0=1.0E2
  KB0=1.0E2
  KP0=1.0E2
  KD0=1.0E2

```

Appendix 5

```
ECRIT=1.0
EPASS=0.5
EACT=3.0E4
KF=KF0*(CL**2.0)*DEXP(0.5*38.92*(298.0/TEMP)*(POT-ECRIT))
KB=KB0*(OH**2.0)*DEXP(0.5*38.92*(298.0/TEMP)*(EPASS-POT))
KP=KP0*DEXP(-EACT/(RGAS*TEMP))
KD=KD0*(POT-ECRIT)
GOTO 100
3 CONTINUE
KF=1.0
KB=1.0
KP=1.0
KD=1.0
IF(POT.GE.ECRIT)GOTO 4
KD=0.0
4 CONTINUE
100 CONTINUE
RETURN
END
```

Appendix 6. Source Code for Figures 16 and 17

```

PROGRAM PIT999K
C*****
C**** STOCHASTIC PROBABILITY MODEL FOR PITTING BY J.C. FARMER ***
C*****
COMMON/A/TEMP,POT,PH,KW,OH,CL,BIRTH,DEATH,TRANS,GRWTH,DZDT,TAU,DT
REAL*4 TEMP,POT,PH,KW,OH,CL,BIRTH,DEATH,TRANS,GRWTH,DZDT,TAU,DT
COMMON/B/NFLAG,BIRTH0,DEATH0,TRANS0,GRWTH0,TAU0,DZDT0
REAL*4 BIRTH0,DEATH0,TRANS0,GRWTH0,TAU0,DZDT0
COMMON/C/ECORR,ECRIT,EPASS
REAL*4 ECORR,ECRIT,EPASS
REAL*4 RR,SUMRR,TOTRR,AVGRR
REAL*4 TIME
REAL*4 AGE0(100,100),AGE1(100,100),AGE2(100,100),DEPTH(100,100)
REAL*4 RATEV,RATEE,RATES
REAL*4 SUMD,DMIN,DAVG,DMAX,SUM(100),Z(100,100)
REAL*4 ALPHA0,ALPHA
INTEGER*4 NV(100,100),NE(100,100),NS(100,100),ND(100,100)
INTEGER*4 NTV0,NTE0,NTS0,NTV,NTE,NTS
C**** OPENING DATA FILE FOR OUTPUT
OPEN(UNIT=1,FILE='DAT999K1.DAT',STATUS='NEW')
OPEN(UNIT=2,FILE='DAT999K2.DAT',STATUS='NEW')
OPEN(UNIT=3,FILE='DAT999K3.DAT',STATUS='NEW')
C**** BANNER OUTPUT TO MONITOR
PRINT *, '*****'
PRINT *, '*** CODE FOR STOCHASTIC PITTING BY J.C.FARMER,LLNL ***'
PRINT *, '*** BASED ON THEORY OF SHIBATA; HENSHAW ARTICLE; ***'
PRINT *, '*** AND MECHANISTIC DEVELOPMENT BY J.C. FARMER ***'
PRINT *, '*** ALL RIGHTS RESERVED - COPYRIGHT - 1997 ***'
PRINT *, '*****'
C**** DEFAULT VALUES OF ENVIRONMENTAL PARAMETERS FOR STOCHASTIC MODEL
C**** REFERENCE: ALLOY 825 TABLE 1 & FIGURE 13 UCID-125300
TEMP=90
POT=0.6432
PH=2.57
CL=50000
C**** DEFAULT VALUES OF ALLOY PARAMETERS FOR STOCHASTIC MODEL
C**** REFERENCE: SS316 TABLE 1 UCID-21362 VOL.3 (SCE SCALE)
ECORR=-0.280
ECRIT=0.230
EPASS=0.0
C**** DEFAULT VALUES OF ADJUSTABLE PARAMETERS
NFLAG=3
BIRTH0=0.30
BIRTH0=0.20
DEATH0=0.20
DEATH0=0.50
TRANS0=0.10
TRANS0=0.05
GRWTH0=0.10
DZDT0=3.0E-04
TAU0=1.0

```

Appendix 6

```

DT=1.0
C**** DEFAULT VALUE FOR TIME STEPS
NK=240
C**** ACCEPT OR REJECT DEFAULT VALUES OF ADJUSTABLE PARAMETERS
WRITE(*,6000)
6000 FORMAT(2X,'ENTER (999) FOR DEFAULT      =' '\)
READ(*,*)IXXX
IF(IXXX.EQ.999)GOTO 9800
7000 CONTINUE
C**** INPUT ENVIRONMENTAL CONDITIONS
WRITE(*,8100)
8100 FORMAT(2X,'TEMPERATURE (DEGREES CENTIGRADE)  =' '\)
READ(*,*)TEMP
WRITE(*,8200)
8200 FORMAT(2X,'PH (DIMENSIONLESS)              =' '\)
READ(*,*)PH
WRITE(*,8300)
8300 FORMAT(2X,'CHLORIDE (PPM)                   =' '\)
READ(*,*)CL
WRITE(*,8400)
8400 FORMAT(2X,'POTENTIAL (VOLTS VS SCE)          =' '\)
READ(*,*)POT
WRITE(*,8500)
8500 FORMAT(2X,'CORROSION POTENTIAL (VOLTS VS SCE) =' '\)
READ(*,*)ECORR
WRITE(*,8600)
8600 FORMAT(2X,'PITTING POTENTIAL (VOLTS VS SCE)  =' '\)
READ(*,*)ECRIT
WRITE(*,8700)
8700 FORMAT(2X,'REPASSIVE POTENTIAL (VOLTS VS SCE) =' '\)
READ(*,*)EPASS
C**** INPUT ADJUSTABLE MODEL PARAMETERS
WRITE(*,9100)
9100 FORMAT(2X,'MODEL (1,2,3)                    =' '\)
READ(*,*)NFLAG
WRITE(*,9200)
9200 FORMAT(2X,'BIRTH0 (EVENTS/TIME OR PROBABILITY) =' '\)
READ(*,*)BIRTH0
WRITE(*,9300)
9300 FORMAT(2X,'DEATH0 (EVENTS/TIME OR PROBABILITY) =' '\)
READ(*,*)DEATH0
WRITE(*,9400)
9400 FORMAT(2X,'TRANS0 (EVENTS/TIME OR PROBABILITY) =' '\)
READ(*,*)TRANS0
WRITE(*,9500)
9500 FORMAT(2X,'GRWTH0 (EVENTS/TIME OR PROBABILITY) =' '\)
READ(*,*)GRWTH0
WRITE(*,9550)
9550 FORMAT(2X,'PENETRATION RATE (DEPTH/TIME)     =' '\)
READ(*,*)DZDT0
WRITE(*,9600)
9600 FORMAT(2X,'TAU0 (TIME)                       =' '\)
READ(*,*)TAU0
WRITE(*,9700)

```

Appendix 6

```

9700 FORMAT(2X,'DT (TIME/STEP)          =' '\)
      READ(*,*)DT
      WRITE(*,9750)
9750 FORMAT(2X,'TIME STEPS              =' '\)
      READ(*,*)NK
9800 CONTINUE
C**** ECHO INPUT FOR POSSIBLE CORRECTIONS
      PRINT *, 'BIRTH0 (EVENTS/TIME OR PROBABILITY) = ',BIRTH0
      PRINT *, 'DEATH0 (EVENTS/TIME OR PROBABILITY) = ',DEATH0
      PRINT *, 'TRANS0 (EVENTS/TIME OR PROBABILITY) = ',TRANS0
      PRINT *, 'GRWTH0 (EVENTS/TIME OR PROBABILITY) = ',GRWTH0
      PRINT *, 'TAU0 (TIME)                =' 'TAU0
      PRINT *, 'DT (TIME/STEP)            =' 'DT
      PRINT *, 'TIME STEPS                 =' 'NK
      PRINT *, 'TEMPERATURE (DEGREES CENTIGRADE) =' 'TEMP
      PRINT *, 'PH (DIMENSIONLESS)         =' 'PH
      PRINT *, 'CHLORIDE (PPM)             =' 'CL
      PRINT *, 'POTENTIAL (VOLTS VS SCE)   =' 'POT
      PRINT *, 'CORROSION POTENTIAL (VOLTS VS SCE) =' 'ECORR
      PRINT *, 'PITTING POTENTIAL (VOLTS VS SCE) =' 'ECRIT
      PRINT *, 'REPASSIVATION POT (VOLTS VS SCE) =' 'EPASS
      WRITE(*,9900)
9900 FORMAT(2X,'ENTER (999) TO ACCEPT VALUES =' '\)
      READ(*,*)IXXX
      IF(IXXX.NE.999)GOTO 7000
C**** OUTPUT ADJUSTABLE PARAMETERS TO ARCHIEVE FILE
      WRITE(1,9950)
      WRITE(1,9951)BIRTH0
      WRITE(1,9952)DEATH0
      WRITE(1,9953)TRANS0
      WRITE(1,9954)GRWTH0
      WRITE(1,9955)TAU0
      WRITE(1,9956)DT
      WRITE(1,9957)TEMP
      WRITE(1,9958)PH
      WRITE(1,9959)CL
      WRITE(1,9960)POT
      WRITE(1,9961)ECORR
      WRITE(1,9962)ECRIT
      WRITE(1,9963)EPASS
9950 FORMAT(1X,'AS INPUT *****')
9951 FORMAT(1X,'BIRTH0 (EVENTS/TIME OR PROBABILITY) = ',E12.6)
9952 FORMAT(1X,'DEATH0 (EVENTS/TIME OR PROBABILITY) = ',E12.6)
9953 FORMAT(1X,'TRANS0 (EVENTS/TIME OR PROBABILITY) = ',E12.6)
9954 FORMAT(1X,'GRWTH0 (EVENTS/TIME OR PROBABILITY) = ',E12.6)
9955 FORMAT(1X,'TAU0 (TIME)                =' 'E12.6)
9956 FORMAT(1X,'DT (TIME/STEP)            =' 'E12.6)
9957 FORMAT(1X,'TEMP (DEGREES CENTIGRADE) =' 'E12.6)
9958 FORMAT(1X,'PH (DIMENSIONLESS)         =' 'E12.6)
9959 FORMAT(1X,'CL (PPM)                   =' 'E12.6)
9960 FORMAT(1X,'POT (VOLTS VS SCE)         =' 'E12.6)
9961 FORMAT(1X,'ECORR (VOLTS VS SCE)       =' 'E12.6)
9962 FORMAT(1X,'ECRIT (VOLTS VS SCE)      =' 'E12.6)
9963 FORMAT(1X,'EPASS (VOLTS VS SCE)      =' 'E12.6)

```


Appendix 6

```

C**** CONVERSION OF ENVIRONMENTAL PARAMETER INPUT VALUES
  TEMP=TEMP+273.0
  CL=CL*(1.0E-03)/(58.44277)
C**** CONVERSION OF PITTING & REPASSIVATION FROM SCE TO NHE
  POT=POT-0.2412
  ECORR=ECORR-0.2412
  ECRIT=ECRIT-0.2412
  EPASS=EPASS-0.2412
C**** INITIALIZE RANDOM NUMBER GENERATOR
  KK=1
  SUMRR=0.0
  TOTRR=0.0
  AVGRR=0.0
  CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
C**** CALCULATE MAX BIRTH, DEATH, & GROWTH PROBABILITIES
  TIME=0.0
C**** CALCULATION OF PITTING PROBABILITIES BASED UPON INPUT
  CALL PROBABLE
C**** OUTPUT RESULTS OF INITIAL CALCULATION TO MONITOR & DATA FILE
  PRINT *, 'INITIAL TIME (TIME)          = ',TIME
  PRINT *, 'TEMPERATURE (KELVINS)        = ',TEMP
  PRINT *, 'PH (DIMENSIONLESS)           = ',PH
  PRINT *, 'CHLORIDE (MOLES/LITER)        = ',CL
  PRINT *, 'POTENTIAL (VOLTS VS NHE)      = ',POT
  PRINT *, 'CORROSION POTENTIAL (VOLTS VS NHE) = ',ECORR
  PRINT *, 'PITTING POTENTIAL (VOLTS VS NHE) = ',ECRIT
  PRINT *, 'REPASSIVATION POT (VOLTS VS NHE) = ',EPASS
  PRINT *, 'BIRTH (EVENTS/TIME OR PROBABILITY) = ',BIRTH
  PRINT *, 'DEATH (EVENTS/TIME OR PROBABILITY) = ',DEATH
  PRINT *, 'TRANS (EVENTS/TIME OR PROBABILITY) = ',TRANS
  PRINT *, 'GRWTH (EVENTS/TIME OR PROBABILITY) = ',GRWTH
  PRINT *, 'PENETRATION RATE (DEPTH/TIME)   = ',DZDT
  PRINT *, 'TAU (TIME)                     = ',TAU
C**** OUTPUT ADJUSTABLE PARAMETERS TO ARCHIEVE FILE
  WRITE(1,1000)
  WRITE(1,1001)BIRTH0
  WRITE(1,1002)DEATH0
  WRITE(1,1003)TRANS0
  WRITE(1,1004)GRWTH0
  WRITE(1,1005)TAU0
  WRITE(1,1006)DT
  WRITE(1,1007)TEMP
  WRITE(1,1008)PH
  WRITE(1,1009)CL
  WRITE(1,1010)POT
  WRITE(1,1011)ECORR
  WRITE(1,1012)ECRIT
  WRITE(1,1013)EPASS
1000 FORMAT(1X,'AFTER UNIT CONVERSIONS ***** ')
1001 FORMAT(1X,'BIRTH0 (EVENTS/TIME OR PROBABILITY) = ',E12.6)
1002 FORMAT(1X,'DEATH0 (EVENTS/TIME OR PROBABILITY) = ',E12.6)
1003 FORMAT(1X,'TRANS0 (EVENTS/TIME OR PROBABILITY) = ',E12.6)
1004 FORMAT(1X,'GRWTH0 (EVENTS/TIME OR PROBABILITY) = ',E12.6)
1005 FORMAT(1X,'TAU0 (TIME)                        = ',E12.6)

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Appendix 6

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1006 FORMAT(1X,DT (TIME) =',E12.6)
1007 FORMAT(1X,TEMP (KELVINS) =',E12.6)
1008 FORMAT(1X,PH (DIMENSIONLESS) =',E12.6)
1009 FORMAT(1X,CL (MOLES/LITER) =',E12.6)
1010 FORMAT(1X,POT (VOLTS VS NHE) =',E12.6)
1011 FORMAT(1X,ECORR (VOLTS VS NHE) =',E12.6)
1012 FORMAT(1X,ECRIT (VOLTS VS NHE) =',E12.6)
1013 FORMAT(1X,EPASS (VOLTS VS NHE) =',E12.6)
C**** INITIALIZE NUMBER OF VACANCIES, EMBRYOS, & STABLE PITS
    NTV=NI*NJ
    NTE=0
    NTS=0
C**** SPECIFICATION OF NUMBER OF CELLS (AREA)
    NI=100
    NJ=100
C**** INITIALIZE EMBRYO & SUSTAINED GROWTH COUNT
    DO 2 J=1,NJ
    DO 1 I=1,NI
    NV(I,J)=1
    NE(I,J)=0
    NS(I,J)=0
    ND(I,J)=0
    1 DEPTH(I,J)=0.0
    2 CONTINUE
C**** WRITE HEADING TO OUTPUT FILE
    WRITE(2,2000)
    2000 FORMAT(7X,'TIME',1X,'VACANCY',2X,'EMBRYO',4X,'PITS',5X,'PIT RATE')
C**** INITIALIZATION OF TIME
    TIME=0.0
C**** OUTER LOOP - BEGIN TIME STEPS
    DO 300 K=1,NK
C**** INITIALIZE NUMBER OF VACANCIES, EMBRYOS, & STABLE PITS
    NTV0=NTV
    NTE0=NTE
    NTS0=NTS
    SUMV=0
    SUME=0
    SUMS=0
    TIME=K*DT
C**** CALCULATE BIRTH, DEATH, & GROWTH PROBABILITIES, ETC.
C**** OPTION 1: BIRTH PROBABILITY DECAYS EXPONENTIALLY WITH TIME
    CALL PROBABLE
    ALPHA0=240.0
    ALPHA=EXP(-TIME/ALPHA0)
C**** OPTION 2: BIRTH PROB DECAYS WITH NUMBER OF EMBRYOS & PITS
    ALPHA0=1.0
    ALPHA=ALPHA0*(10000.0-NTE-NTS)/10000.0
C**** OPTION 3: BIRTH PROB PASSES THROUGH TIME-DEPENDENT MAXIMUM
    ALPHA0=TIME/10.0
    ALPHA=ALPHA0*(10000.0-NTE-NTS)/10000.0
C**** OPTION 4: BIRTH PROB PASSES THROUGH SURFACE-DEPENDENT MAXIMUM
    ALPHA0=(10000.0-NTE-NTV)/10000.0
    ALPHA=ALPHA0*(10000.0-NTE-NTS)/10000.0
C**** CALCULATION OF DECAY IN BIRTH PROBABILITY

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      BIRTH=ALPHA*BIRTH
C**** SCANNING I-J CELLS FOR EVENTS DURING K-TH TIME STEP
      DO 200 J=1,NJ
      DO 100 I=1,NI
C**** DETECT STABLE PIT
      IF(NS(I,J).EQ.1)GOTO 50
C**** DETECT VACANCY
      IF(NV(I,J).EQ.1.AND.NE(I,J).EQ.0)GOTO 60
C**** DETECT EMBRYO
      IF(NV(I,J).EQ.0.AND.NE(I,J).EQ.1)GOTO 70
C**** THE PROGRAM SHOULD NOT COME DIRECTLY TO THIS POINT
      PRINT *, ' STATE DETECTION ERROR!'
C**** CELL CALCULATIONS FOR DETECTED STABLE PIT
      50 CONTINUE
      AGE2(I,J)=TIME-AGE1(I,J)
      CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
      IF(RR.LE.GRWTH.OR.ND(I,J).EQ.1)GOTO 51
      GOTO 52
      51 CONTINUE
C**** THE STABLE PIT CEASES TO GROW (DEATH OF STABLE PIT)
      NV(I,J)=0
      NE(I,J)=0
      NS(I,J)=1
      ND(I,J)=1
      DEPTH(I,J)=DEPTH(I,J)
      52 CONTINUE
C**** THE STABLE PIT CONTINUES TO GROW
      NV(I,J)=0
      NE(I,J)=0
      NS(I,J)=1
      ND(I,J)=0
      IF(DEPTH(I,J).EQ.0.0)GOTO 53
C**** THE GROWTH RATE FOR PIT DEPTH IS A FUNCTION OF DEPTH
      DREF=0.05
      DEPTH(I,J)=DEPTH(I,J)+DT*DZDT*DREF/DEPTH(I,J)
      GOTO 54
      53 CONTINUE
      DEPTH(I,J)=DEPTH(I,J)+DT*DZDT
      54 CONTINUE
      GOTO 90
C**** CELL CALCULATIONS FOR DETECTED VACANCY
      60 CONTINUE
      CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
C**** DETECTION OF EMBRYO BIRTH
      IF(RR.LE.BIRTH)GOTO 61
      GOTO 90
      61 NV(I,J)=0
      NE(I,J)=1
      NS(I,J)=0
      ND(I,J)=0
      AGE0(I,J)=TIME
      GOTO 90
C**** CELL CALCULATIONS FOR DETECTED EMBRYO
C**** DETECTION OF CRITICAL AGE

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Appendix 6

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70 CONTINUE
  AGE=TIME-AGE0(I,J)
  CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
  IF(RR.LE.TRANS.AND.AGE.GE.TAU)GOTO 71
  GOTO 80
71 NV(I,J)=0
  NE(I,J)=0
  NS(I,J)=1
  ND(I,J)=0
  AGE1(I,J)=AGE0(I,J)
  GOTO 90
C**** CELL CALCULATIONS FOR DETECTED EMBRYO
C**** DETECTION OF EMBRYO DEATH
80 CONTINUE
  CALL RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)
  IF(RR.LE.DEATH)GOTO 72
  GOTO 90
72 NV(I,J)=1
  NE(I,J)=0
  NS(I,J)=0
  ND(I,J)=0
C**** DETECTION COMPLETED
90 CONTINUE
C**** EMBRYO & PIT SUMMATION
  SUMV=SUMV+NV(I,J)
  SUME=SUME+NE(I,J)
  SUMS=SUMS+NS(I,J)
100 CONTINUE
200 CONTINUE
C**** END OF I-J CELL SCANNING
C**** TOTAL EMBRYOS & STABLE PITS COUNTED DURING K-TH TIME STEP
  NTV=SUMV
  NTE=SUME
  NTS=SUMS
C**** CALCULATION OF EMBRYO, DEATH & PITTING RATES
  RATEV=(NTV-NTV0)/(NI*NJ*DT)
  RATEE=(NTE-NTE0)/(NI*NJ*DT)
  RATES=(NTS-NTS0)/(NI*NJ*DT)
C**** OUTPUT RESULTS
  PRINT *,TIME,NTV,NTE,NTS,RATES
  WRITE(2,2001)TIME,NTV,NTE,NTS,RATES
2001 FORMAT(1X,F10.4,3(2X,I6),1X,E12.6)
300 CONTINUE
C**** DETECTION OF THE MINIMUM, MAXIMUM & MEAN PIT DEPTH
  DMAX=0.0
  DMIN=1.0E9
  SUMD=0.0
  SIZE=0.0
  DO 650 J=1,NJ
  DO 650 I=1,NI
  IF(NS(I,J).EQ.0.0)GOTO 650
  IF(DMIN.LE.DEPTH(I,J))GOTO 600
  DMIN=DEPTH(I,J)
  GOTO 620

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Appendix 6

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600 CONTINUE
  IF(DMAX.GE.DEPTH(I,J))GOTO 610
  DMAX=DEPTH(I,J)
  GOTO 620
610 CONTINUE
  SUMD=SUMD+DEPTH(I,J)
620 SIZE=SIZE+1.0
650 CONTINUE
  IF(SIZE.EQ.0.0)GOTO 660
  DAVG=SUMD/SIZE
  GOTO 670
660 PRINT *, ' ERROR IN ESTABLISHING PIT SIZE DISTRIBUTION!'
670 CONTINUE
  PRINT *, ' SIZE=',SIZE
  PRINT *, ' DMIN=',DMIN
  PRINT *, ' DAVG=',DAVG
  PRINT *, ' DMAX=',DMAX
  WRITE(3,3001)SIZE
  WRITE(3,3002)DMIN
  WRITE(3,3003)DAVG
  WRITE(3,3004)DMAX
  WRITE(3,3005)
3001 FORMAT(1X,'SIZE=',E10.4)
3002 FORMAT(1X,'DMIN=',E10.4)
3003 FORMAT(1X,'DAVG=',E10.4)
3004 FORMAT(1X,'DMAX=',E10.4)
3005 FORMAT(1X,'DEPTH(%DMAX)',1X,'PROBABILITY(%)')
C**** FORMATION OF THE PROBABILITY DISTRIBUTION FUNCTION FOR PIT DEPTHS
  DO 700 K=1,100
700 SUM(K)=0.0
  DO 710 J=1,NJ
  DO 710 I=1,NI
    Z(I,J)=DEPTH(I,J)*100.0/DMAX
    INDEX=Z(I,J)
    SUM(INDEX)=SUM(INDEX)+1
710 CONTINUE
  DO 720 K=1,100
    SUM(K)=100.0*SUM(K)/SIZE
    PRINT *, ' PERCENT OF MAX DEPTH = ',K, ' PROBABILITY = ',SUM(K)
    WRITE(3,3006)K,SUM(K)
3006 FORMAT(7X,I4,5X,F10.4)
720 CONTINUE
  PRINT *, ' TOTAL RANDOM NUMBERS GENERATED =',TOTRR
  PRINT *, ' AVERAGE OF ALL RANDOM NUMBERS =',AVGRR
  WRITE(1,1014)
1014 FORMAT(1X,'*****')
  WRITE(1,1015)TOTRR
1015 FORMAT(1X,'TOTAL RANDOM NUMBERS GENERATED   =',E12.6)
  WRITE(1,1016)AVGRR
1016 FORMAT(1X,'AVERAGE OF RANDOM NUMBERS GENERATED =',E12.6)
  STOP
  END

  SUBROUTINE RANDOM(KK,RR,SUMRR,TOTRR,AVGRR)

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Appendix 6

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C*****
C*****RANDOM NUMBER ALGORITHM FROM MANUAL OF HP-20S SCIENTIFIC CALC ***
C*****SUBROUTINE WRITTEN BY J.C. FARMER APRIL 6, 1997 *****
C*****
      REAL*4 RR,SUMRR,TOTRR,AVGRR
      IF(KK.GT.1)GOTO 20
C*****RANDOM NUMBER SEED FOR GENERATOR
      RR=0.5284163
      20 CONTINUE
C*****RESET COUNTER
C*****COMPUTATION OF RANDOM NUMBER BY ADDITIVE TECHNIQUE
      RR=997*RR
      JJ=RR
      RR=RR-JJ
C*****CALCULATION FO THE AVERAGE OF RANDOM NUMBERS
      SUMRR=SUMRR+RR
      TOTRR=TOTRR+1.0
      AVGRR=SUMRR/TOTRR
      KK=KK+1
      RETURN
      END

      SUBROUTINE PROBABLE
C**** CALC OF BIRTH, DEATH, TRANS, & GROWTH PROB; CRITICAL TIME
C**** CALCULATION BY (A) HENSHALL & SHIBATA; (B) FARMER & HENSHALL
      COMMON/A/TEMP,POT,PH,KW,OH,CL,BIRTH,DEATH,TRANS,GRWTH,DZDT,TAU,DT
      REAL*4 TEMP,POT,PH,KW,OH,CL,BIRTH,DEATH,TRANS,GRWTH,DZDT,TAU,DT
      COMMON/B/NFLAG,BIRTH0,DEATH0,TRANS0,GRWTH0,TAU0,DZDT0
      REAL*4 BIRTH0,DEATH0,TRANS0,GRWTH0,TAU0,DZDT0
      COMMON/C/ECORR,ECRIT,EPASS
      REAL*4 ECORR,ECRIT,EPASS
      IF(NFLAG.EQ.1)GOTO 1
      IF(NFLAG.EQ.2)GOTO 2
      IF(NFLAG.EQ.3)GOTO 3
C**** CALCULATED RATES AS PER HENSHALL ARTICLE
C**** CONDITIONS FROM TABLE 3 FIGURE 9B OF HENSHALL ARTICLE
      1 CONTINUE
      RGAS=8.314
      A1=6.164E12
      A2=4.856
      A3=2.7E-4
      A4=2.0E-4
      B1=0.4
      B3=0.4
      B4=0.4
      B5=0.5
      C1=1.0
      C2=0.2
      C3=0.2
      C4=1.1
      ACT1=2.27E4
      ACT2=1600.
      ACT3=750.
      ACT4=1.00E4

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Appendix 6

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BIRTH1=A1*(POT-B1)*DEXP(C1*CL)*DEXP(-ACT1/(RGAS*TEMP))
DEATH1=A2*DEXP(-C2*CL)*DEXP(-ACT2/(RGAS*TEMP))
TRANS1=1.0E03
GRWTH1=A4*((POT-B4)**B5)*(CL**C4)*DEXP(ACT4/(RGAS*TEMP))
DZDT1 =DZDT0
TAU1 =A3*DEXP(-B3*POT)*DEXP(-C3*CL)*DEXP(ACT3/(RGAS*TEMP))
C**** FARMER'S CHARGE-TRANSFER MECHANISTIC MODEL FOR RATES
C**** ALSO SEE UCID-21362 VOL. 3 EQN. 7 (OKADA'S MODEL FOR TAU)
2 CONTINUE
RGAS=8.314
KW=1.0E-14
OH=KW/(10.0**(-PH))
D1=0.5
D2=0.5
D3=2.0
EACT1=3.0E4
EACT2=3.0E4
BIRTH1=BIRTH0*(CL**2.0)*DEXP(D1*38.92*(298.0/TEMP)*(POT-ECRIT))
DEATH1=DEATH0*(OH**2.0)*DEXP(D2*38.92*(298.0/TEMP)*(EPASS-POT))
TRANS1=TRANS0*DEXP(-EACT1/(RGAS*TEMP))
GRWTH1=GRWTH0
DZDT1 =DZDT0
TAU1 =TAU0*(CL**4.0)/DEXP(D3*38.92*(298.0/TEMP)*(POT-ECRIT))
100 CONTINUE
C**** CALCULATION OF BOUNDED PROBABILITIES AS PER SHIBATA ET AL.
C**** SEE EQN. 63 OF CORROSION, VOL. 52, NO. 11, PP. 813-830.
BIRTH=1.0-DEXP(-DT*BIRTH1)
DEATH=1.0-DEXP(-DT*DEATH1)
TRANS=1.0-DEXP(-DT*TRANS1)
GRWTH=1.0-DEXP(-DT*GRWTH1)
DZDT =DZDT1
TAU =TAU1
GOTO 4
C**** DEFAULT VALUES OF PROBABILITIES
3 CONTINUE
BIRTH=BIRTH0
DEATH=DEATH0
TRANS=TRANS0
GRWTH=GRWTH0
DZDT=DZDT0
TAU=TAU0
4 CONTINUE
RETURN
END

```

Appendix 6

Input Data for Source Code

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AS INPUT *****
BIRTH0 (EVENTS/TIME OR PROBABILITY) = .200000E+00
DEATH0 (EVENTS/TIME OR PROBABILITY) = .500000E+00
TRANS0 (EVENTS/TIME OR PROBABILITY) = .500000E-01
GRWTH0 (EVENTS/TIME OR PROBABILITY) = .100000E+00
TAU0 (TIME) = .100000E+01
DT (TIME/STEP) = .100000E+01
TEMP (DEGREES CENTIGRADE) = .900000E+02
PH (DIMENSIONLESS) = .257000E+01
CL (PPM) = .500000E+05
POT (VOLTS VS SCE) = .643200E+00
ECORR (VOLTS VS SCE) = -.280000E+00
ECRIT (VOLTS VS SCE) = .230000E+00
EPASS (VOLTS VS SCE) = .000000E+00
AFTER UNIT CONVERSIONS *****
BIRTH0 (EVENTS/TIME OR PROBABILITY) = .200000E+00
DEATH0 (EVENTS/TIME OR PROBABILITY) = .500000E+00
TRANS0 (EVENTS/TIME OR PROBABILITY) = .500000E-01
GRWTH0 (EVENTS/TIME OR PROBABILITY) = .100000E+00
TAU0 (TIME) = .100000E+01
DT (TIME) = .100000E+01
TEMP (KELVINS) = .363000E+03
PH (DIMENSIONLESS) = .257000E+01
CL (MOLES/LITER) = .855538E+00
POT (VOLTS VS NHE) = .402000E+00
ECORR (VOLTS VS NHE) = -.521200E+00
ECRIT (VOLTS VS NHE) = -.112000E-01
EPASS (VOLTS VS NHE) = -.241200E+00
*****
TOTAL RANDOM NUMBERS GENERATED = .245023E+07
AVERAGE OF RANDOM NUMBERS GENERATED = .500093E+00

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