



Unification of the deterministic and statistical approaches for predicting localized corrosion damage.

I. Theoretical foundation

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Abstract

In this paper, we provide an alternative, more general theoretical basis for damage function analysis (DFA), by drawing an analogy between the growth of a pit and the movement of a particle. In contrast to our previous formulation of DFA, which was developed specifically for enabling the damage function for localized corrosion to be calculated from the point defect model for passivity breakdown, the coupled environment pitting model for pit growth, and the theory of prompt and delayed repassivation, the new formulation readily incorporates any theories or models (deterministic or empirical) for these stages in the development of a pit. We show that the new formulation leads to the original expressions for the damage functions for active (living) and passivated (dead) pits, and hence for the differential and integral damage functions, as were obtained from the original theory. We also describe the unification of deterministic (damage function analysis, DFA) and empirical, statistical (extreme value statistics, EVS) methods for predicting the development of localized corrosion damage on metal surfaces. In particular, we have devised a means of estimating the central and scale parameters of EVS directly from DFA in a “first principles” manner, as well as from fitting the EVS distribution function to experimental data for short times, in order to predict the extreme value distributions at longer times. The techniques have been evaluated on EVS data for the pitting of manganese steel in CO₂-acidified seawater and for the pitting of aluminum in tap

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water. Finally, we outline the generalization of pit nucleation, as described by the point defect model, for external conditions that depend on time.

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1. Introduction

The development of effective localized corrosion damage prediction technologies is essential for the successful avoidance of unscheduled downtime in industrial systems and for the successful implementation of life extension strategies. Currently, corrosion damage is extrapolated to future times by using various empirical models coupled with damage tolerance analysis (DTA). In this strategy, known damage is surveyed during each subsequent outage, and the damage is extrapolated to the next inspection period allowing for a suitable safety margin. It has been noted previously [1] that this strategy is inherently inaccurate and inefficient, and that in many instances it is too conservative. Instead, it has been suggested that damage function analysis (DFA) is a more effective method for predicting the progression of damage, particularly when combined with periodic inspection [1]. Although corrosion is generally complicated mechanistically, a high level of determinism has been achieved in various treatments of both general and localized corrosion, which can be used to predict accumulated damage in the absence of large calibrating databases [2].

It is important to note that the word “determinism” is used here to describe a model that contains a physically viable mechanism (i.e., one that accounts for the known properties of the system) and whose predictions along the system’s evolutionary path are constrained by the natural laws. The great majority of models that are used in corrosion science and engineering do not satisfy the definition of determinism given above and indeed many are little more than sophisticated correlations. However, many statistical models, such as those contained within extreme value statistics (EVS), make no pretense of being mechanistically-based or of conforming to the constraints of determinism, yet they have proven to be of great utility in correlating experimental data in terms of relationships between the dependent and independent variables. Generally speaking, the traditional statistical approach that is used for extrapolating corrosion damage in time (and space) can be described as follows [3]. It is assumed that the distribution of the deepest pits on many specimens for a given observation time is described by one of the three classical extreme value distributions that are functions of two or three statistical parameters (central, u , scale, α , and a shape parameter, k). Empirical expressions are developed for parameters u , α , and k by assuming functional dependencies on time, t , which are then used to extrapolate the parameters to longer times (and often to larger area). Thus, in Ref. [3], it is assumed that $u = u_0 t^b$ and $\alpha = \alpha_0 t^b$, with the same power, b , and that $k = \text{const}$, but there is no physical justification for the selection. In this approach, the fitting parameters u_0 , α_0 , b , and k are not related to the physical parameters of the corrosion system, such as pit propagation rate, repassivation

constant, etc. Accordingly, in using such an approach, it is, in principle, impossible to predict corrosion damage for a system beyond the experimental field, particularly if the external conditions depend on time. Moreover, presentation of the central and scale parameters in the form of power functions renders impossible the prediction of damage when the depth of the deepest pit cannot increase beyond some critical value (e.g., due to repassivation of the pit) [4]. These models should not be termed “predictive”, since they all contain parameters (e.g., the central and scale parameters in the Gumbel Type I distribution function in EVS) for which there is no deterministic guidance as to their values and future time dependencies. This specific issue is addressed in the present paper.

As previously noted [1,5], the evolution of localized corrosion damage is a birth (nucleation)–growth (propagation)–death (repassivation) process, in which these stages (birth, growth, and death) occur sequentially for a single event, but tend to occur in parallel for a large ensemble of events. These basic features classify the system as being “progressive”, because new, damaging events nucleate as existing events live and die. Accordingly, any models that are incorporated into DFA must recognize the progressive nature of the evolution of damage. The progressive nature of the process is captured in the “damage function” (DF), which is the histogram of event frequency versus increment in depth (Fig. 1).

The predicted DFs shown in Fig. 1 for aluminum in chloride solutions [6] represent the distribution in depth of the damaging process (e.g., pitting and/or stress corrosion cracking) for different observation times. The principal value of the DF is that it provides ready definitions of “failure” and the “time to failure”, with the latter being the observation time at which the upper extreme exceeds the critical dimension, L_{cr} . Thus, with regard to Fig. 1, failure would not have occurred after one

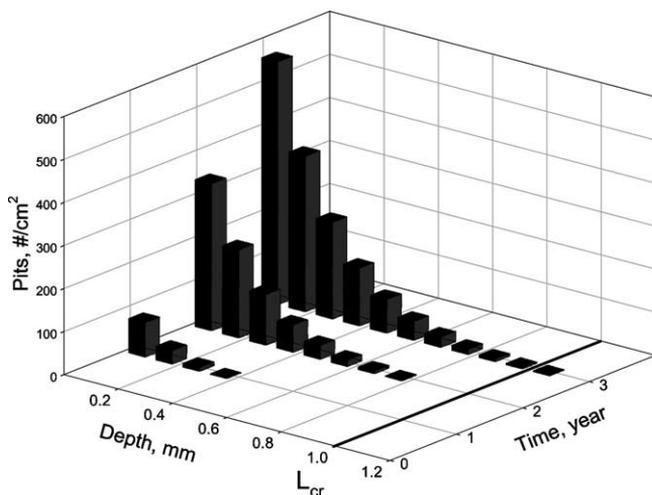


Fig. 1. Examples of predicted damage functions in pit depth for the pitting corrosion of aluminum in chloride solutions for $E_{corr} = -0.384 V_{she}$, $[Cl^-] = 0.002 M$, $pH = 7$, and $\gamma = 3 \text{ year}^{-1}$.

and two years of exposure, but it would have occurred after three. Clearly, prediction of the evolution of the DF with time is the necessary requirement for calculating the time at which a system will fail due to localized corrosion and hence for calculating the failure time. However, the DF also allows one to predict the extent of localized corrosion damage as being the integrated area under the distribution that defines the DF. For many applications, the extent of damage is an important quantity, depending upon the definition of “failure”. For example, corrosion-induced roughening of the surface of a ball bearing will often cause the bearing to fail in a time that is related to the extent of roughening rather than to the maximum depth.

The authors have established the theoretical basis of DFA over the past decade [1,2,5,6], and its utility in predicting localized corrosion damage in a number of systems has been well demonstrated [1,5,6]. In the present work, we develop a new method of calculating the DF, by drawing an analogy between the growth of pits and the transport of particles. This alternative treatment, which is outlined below, leads to the same result as our previous analysis in the simplest case, but it also provides a foundation for quantitatively describing arbitrarily complicated systems, particularly for incorporating multiple modes of damage (pitting, stress corrosion cracking, and corrosion fatigue) into DFA, or for investigating cases when the external conditions (temperature, corrosion potential, electrolyte composition, etc.) depend on time.

While considerable advances have been made in the deterministic prediction of corrosion damage over the past two decades, a strictly deterministic description of the propagation of corrosion damage in a majority of real systems continues to be a major theoretical challenge that is only slowly yielding to scientific inquiry. The difficulties inherent in this task not only reflect the lack of information for various kinetic parameters for the nucleation, repassivation, and propagation of pits, but they also include the frequently poorly defined statistical nature of some corrosion processes, even though the underlying causes are deterministic in nature. For example, we do not adequately understand the statistical nature of the corrosion cavity growth rate in terms of the physico-electrochemical origin of the distribution or its mathematical form, although if this information were available then, at least in principle, the inclusion of the mechanism in a deterministic model is feasible. There exist many possible reasons for a distribution in cavity growth rate, including, example, the spatial distribution in anodic and cathodic sites on the corroding surface or because of microstructural and microchemical non-uniformity of the metal [7,8]. In this paper, we report the first attempt to demonstrate the application of DFA to the case where a distribution exists in the corrosion cavity propagation rate.

For example, it will be shown from DFA that, with certain simplifying assumptions, the distribution of the deepest pit among “identical” specimens must be described by extreme value statistics (EVS). A combination of DFA and traditional statistical analysis (SA) offers significant advantages over purely statistical/empirical approaches that are not based upon deterministic principles. Thus, DFA allows us to express the fitting parameters for SA in terms of values for the physical parameters of the component deterministic model(s) (e.g. pit nucleation and propagation rates, repassivation constants, etc.) that can be validated by independent experiment.

Accordingly, it becomes possible to predict the statistical fitting parameters as the external conditions change with time.

2. Theoretical basis of DFA

Localized corrosion damage in an arbitrary system is completely defined if we know how many pits or other corrosion events (per cm^2) have depths between x_1 and x_2 ($x_1 < x_2$) for a given observation time, t . Let us denote this number by $\Delta N_k(x_1, x_2, t)$. Here, index k denotes different types of corrosion event (e.g., pits or cracks). Instead of employing a function with three variables, ΔN_k , it is more convenient to use a function of two variables—the integral damage function (IDF), $F_k(x, t)$. This function is defined as the number (per cm^2) of corrosion events with depths larger than x for a given observation time, t . It is evident that

$$\Delta N_k(x_1, x_2, t) = F_k(x_1, t) - F_k(x_2, t) \quad (1)$$

In turn, it is convenient to express the integral DF, $F_k(x, t)$, via the differential DF, $f_k(x, t)$, using the relation

$$F_k(x, t) = \int_x^\infty f_k(x', t) dx' \quad \text{or} \quad f_k(x, t) = -\frac{\partial F_k(x, t)}{\partial x} \quad (2)$$

The differential DF for defects of type k , f_k , is defined from the condition that $f_k(x, t) dx$ is the number of defects k (per cm^2) having a depth between x and $x + dx$ for a given observation time, t . It is evident that the set of functions f_k for all types of defects yields complete information about damage in the system. The advantage of using the differential DF lies in the fact that it obeys a simple differential equation (see below) and accordingly can be calculated for any given set of conditions. Of course, all of the functions $\Delta N_k(x_1, x_2, t)$, $F_k(x, t)$, and $f_k(x, t)$ may depend, in the general case, on position on the metal surface, but in this analysis we will assume that all sites belong to a given ethnic population.

The function f_k has dimension of $\# / (\text{cm}^2 \text{cm}) = \# / \text{cm}^3$ (analogous to the concentration of a particle). Accordingly, it is very convenient to regard each defect as a “particle” that moves in the x direction (perpendicular to the surface, with $x = 0$ being at the metal surface). The coordinate of this particle, x , coincides with the depth of penetration of the defect. Accordingly, f_k can be regarded as the concentration of particles and hence must obey the law of mass conservation,

$$\frac{\partial f_k}{\partial t} + \frac{\partial j_k}{\partial x} = R_k, \quad k = 1, 2, \dots, K \quad (3)$$

where j_k and R_k are the flux density and the bulk source (sink) of the “particles” k , respectively. Thus, the subscript “ k ” enumerates the corrosion defect and “ K ” is the total number of different corrosion defects in the system. By definition $R_k(x, t) dx dt$ yields the number of defects k (per cm^2) with depths between x and $x + dx$ that arise (or disappear) during the period of time between t and $t + dt$, due to the transformation (repassivation, in the case of pits).

This new formulation of DFA affords considerable advantage over the previous treatment [1,2,5]: we now possess a method of calculating the DF for a complicated system. To fulfill this task, we must solve the system of equations (3) with the corresponding boundary and initial conditions.

$$j_k = n_k(t) \quad \text{at } x = 0, \quad t > 0 \quad (4)$$

and

$$f_k = f_{k0}(x) \quad \text{at } x > 0, \quad t = 0 \quad (5)$$

where $f_{k0}(x)$ is the initial distribution of defect k (usually we can assume that $f_{k0}(x) = 0$, i.e., no damage exists at zero time) and $n_k(t)$ is the nucleation rate of the same defect (i.e., $n_k(t) dt$ is the number of stable defects (per cm^2) that nucleate in the induction time interval between t and $t + dt$).

Thus, because the defect propagation flux, j_k , must be non-negative (the depth of a corrosion event can only increase with time), the following, simplest numerical upwind finite difference scheme can be used for numerically solving Eqs. (3)–(5).

$$f_{k,m}^{n+1} = f_{k,m}^n - \frac{\Delta t}{\Delta x} (j_{k,m}^n - j_{k,m-1}^n) + R_{k,m}^n \Delta t \quad (6)$$

Here, we use the straightforward approach of choosing equally spaced points along both the t - and x -axes: $x_j = x_0 + m\Delta x$, $m = 0, 1, \dots, J$ and $t_j = t_0 + n\Delta t$, $n = 0, 1, \dots, N$, and we denote $f_{k,m}^n = f_k(t_n, x_m)$. The values $f_{k,0}^n$ and $f_{k,m}^0$ are calculated from the boundary and initial Conditions (4) and (5). Of course, it is assumed that we know (i.e. can calculate) fluxes, j_k , and sources, R_k , as functions of the spatial coordinates and time, and, in the general case, as functions of the unknown values of f_k .

In the simplest cases, it is even possible to obtain analytical solutions for the damage functions. As an example, let us consider the case of pitting corrosion under constant external conditions. In this case, we have two kinds of defect ($K = 2$): active pits with the damage function, f_a , and passivated pits (i.e., those that have “died” through delayed repassivation) with the damage function, f_p . Here, and elsewhere in this paper, subscripts “a” ($k = 1$) and “p” ($k = 2$) denote active and passive pits, respectively.

Let us assume that the rate of pit propagation, V , depends only on the depth of the pit, x . Accordingly, for the flux of active pits, j_a , we have:

$$j_a(x, t) = f_a(x, t)V(x) \quad (7)$$

Generalization of this expression will be done later. However, it worth noting that the expression for the flux density cannot contain “diffusion terms”, because pits can only increase their depth and the flux does not depend on the gradient in the pit population and hence on the differential damage function. By definition, the flux of passivated pits, j_p , is zero (i.e., these pits are “dead”). It is also evident that functions R_a and R_p must obey the relation $R_p = -R_a$, since the rate of appearance of passivated pits must equal the rate of disappearance of active pits, due to passivation, at any given moment in time. If, in addition, we assume that the pit repassivation process

obeys a first-order decay law (the rate of passivation is proportional to the number of active pits), the function R_a has the form

$$R_a(x, t) = -\gamma f_a(x, t) \quad (8)$$

where γ is the delayed repassivation (“death”) constant (i.e., the rate constant for repassivation of stable pits). The negative sign indicates that the number of active pits decreases due to repassivation. In the general case, γ depends on the external conditions and, accordingly, on the depth of the pit, if significant potential and concentration drops exist within the cavity. In addition, γ may also depend on time when the external conditions vary. However, in this example, we assume that γ is a constant and hence that the probability of repassivation does not depend on pit depth. (This is clearly a gross over-simplification, since the probability of delayed repassivation is expected to increase with pit age, but this does not change the logic of the argument.) Accordingly, the system of equations for calculating the DFs has the form

$$\frac{\partial f_a}{\partial t} + \frac{\partial(Vf_a)}{\partial x} = -\gamma f_a \quad (9)$$

and

$$\frac{\partial f_p}{\partial t} = \gamma f_a \quad (10)$$

The boundary and initial conditions are then given as

$$Vf_a = n(t) \text{ at } x = 0, t > 0 \quad \text{and} \quad f_a = f_p = 0 \text{ at } t = 0 \quad (11)$$

The difference between Eqs. (9) and (10) is as follows: Eq. (9) shows that the number of active pits can change due to the nucleation of new pits and the repassivation of existing (active) pits. In contrast, the number of dead pits can change only due to the repassivation of active pits (Eq. (10)).

An analytical solution to the boundary value problem formulated above yields

$$f_a = \frac{\exp[-\gamma\theta(x)]n[t - \theta(x)]}{V(x)} \quad (12)$$

and

$$f_p = \frac{\gamma \exp[-\gamma\theta(x)]N[t - \theta(x)]}{V(x)} \quad (13)$$

where

$$\theta_{\text{pit}}(x) = \int_0^x \frac{dx'}{V(x')} \quad (14)$$

is the age of a pit with depth x and

$$N(t) = \int_0^t n(t') dt' \quad (15)$$

is the number of stable pits (per cm^2) that nucleate in the time interval between 0 and t .

It is important to note that, experimentally, only the sum of the damage functions for active and passive pits, $f = f_a + f_p$, is determined and, in many instances, the integral damage function, $F = F_a + F_p$, only is measured. Accordingly, it is important, for practical reasons, to obtain the equation for the integral damage function. Note that the integral damage function, F , corresponds to the number of remaining pits (active and passive) on a surface, as the surface is removed layer-by-layer in pre-established increments. From Eqs. (2), (12) and (13) we therefore have

$$F(x, t) = \exp[-\gamma\theta(x)]N[t - \theta(x)] \quad (16)$$

According to the theory developed above, calculation of the damage functions requires the determination of three independent functions for each kind of corrosion defect, k : The rate of defect nucleation, n_k , the flux density (growth rate) of the defect, j_k , and the rate of transition of one kind of defect to another, R_k , (for example, the transition of an active pit into a passive pit or the transition of a pit into a crack). Below, we will discuss briefly the feasibility of calculating each of these three functions from first principles.

2.1. Rate of pit nucleation

In many practical cases, it is possible to assume that all pits on a given surface nucleate during an initial period of time that is much less than the observation time, t , or the service life of the system, t_s (instantaneous nucleation). For example, for the case of the pitting corrosion of aluminum in tap water, practically all of the pits were found to nucleate within the first two weeks [9]. Under these conditions, the total number of nucleated stable pits, as a function of time, can be simply represented as

$$N(t) = N_0 U_+(t) \quad (17)$$

where N_0 is the maximum number of the stable pits (per cm^2) that can exist on the metal surface and $U_+(t)$ is the asymmetrical unit function ($U_+ = 0$ at $t \leq 0$ and $U_+ = 1$ at $t > 0$).

If pit nucleation cannot be regarded as being “instantaneous”, the simplest assumption concerning the pit nucleation rate, $n(t) = dN/dt$, is that $n(t)$ is proportional to the number of available sites, $N_0 - N(t)$ [10], which yields

$$N(t) = N_0[1 - \exp(-t/t_0)] \quad (18)$$

where t_0 is some characteristic time that depends on the corrosion potential, temperature, and electrolyte composition.

A more general and sophisticated calculation of the pit nucleation rate can be made in the following way. Although an extensive database does not exist to support this position, it is postulated that the rate of nucleation of stable pits, $n = dN/dt$, is related to the rate of nucleation of metastable pits, $n_{MP} = (dN/dt)_{MP}$, by

$$n(t) = \frac{dN}{dt} = \zeta \left(\frac{dN}{dt} \right)_{\text{MP}} \quad (19)$$

where parameter ζ is termed the survival probability [10–12]. This parameter can be measured experimentally. Thus, for example, for Type 304L stainless steel in NaCl solution, the experimentally measured survival probability has a value of the order of 10^{-2} [12].

For calculating the rate of nucleation of metastable pits, the point defect model (PDM) can be used [13–17]. On the basis of this model, it can be shown that total number of nucleated pits can be described by the following expression [5]:

$$N(t) = N_0 \operatorname{erfc} \left(\frac{a}{t} + b \right) / \operatorname{erfc}(b) \quad (20)$$

Parameters a and b specifically depend on temperature, pH, activity of halide ion, and the metal potential, but do not depend on the induction time. These dependencies can be found in the original work [5,13–17] or in Appendix A of this article. To the best of our knowledge, the PDM is the only model that establishes the connection between pit nucleation rate and the external conditions. For example, in the empirical equation (18), the connection between the parameter, t_0 , and the external conditions (pH, potential, etc.) is not specified. It is interesting to note that, if the observation time, t , satisfies the condition $t \gg a(b + \sqrt{b^2 + 4})/2$, practically all pits nucleate during a very short period of time at the beginning of experiment, i.e. the PDM predicts the limiting case of instantaneous nucleation [5].

However, it is also important to note that the original PDM describes pit nucleation for the case when the external conditions do not depend on time. This restriction can be a serious impediment in predicting the pit nucleation rate under practical conditions, for example, when seasonal changes in temperature and wetness are observed for a system that is subject to atmospheric corrosion. However, the PDM is easily generalized for the case of variable external conditions, as described in Appendix A.

2.2. Rate of pit propagation

The quantitative description of pit (or crack) growth can be regarded as one of the key problems in predicting corrosion damage in many practical systems. This follows from the fact that the calculated corrosion damage that is based only on this (growth) stage can be compared with experiment, in many limiting cases. For example when all pits nucleate “instantaneously”, or when the induction time for pit nucleation is much smaller than the observation time, it is possible to ignore the initial stage of pit nucleation when estimating the damage. In addition, if the probability of survival of a corrosion defect is sufficiently high, we must take into account the possibility that a stable corrosion defect (pit or crack) nucleates immediately after the start of operation and propagates without repassivation. In any case, calculations based only on the growth stage yield the most conservative estimate of the service life, $t_{s,\min}$, of the system. We can be sure that, if calculation of

the service life is based on growth alone, the real service life, t_s , will at least be not less than $t_{s,\min}$.

It is well known from both experiment [18] and theory [19] that the dependence of the characteristic dimension of a corrosion cavity (for example, cavity depth, L) on time, t , can be expressed by a simple equation of the following form:

$$L = kt^m \quad (21)$$

where k and m are empirical constants, and, usually, $m \leq 1$. However, this dependence of L on t cannot be used directly in mathematical calculations for small times, because of the non-physical limit

$$V = \frac{dL}{dt} = kmt^{m-1} \rightarrow \infty, \quad \text{at } t \rightarrow 0 \quad \text{and} \quad m < 1 \quad (22)$$

This is why, instead of Eq. (21), we use the following interpolation equation for pit propagation rate:

$$V = \frac{dL}{dt} = V_0(1 + t/t_0)^n \quad (23)$$

where $n = m - 1$ and t_0 are constants, and V_0 is the initial, finite rate of pit propagation. Eq. (23) yields $V = V_0$ at $t/t_0 \ll 0$ and $V = V(t/t_0)^n$ at $t \gg t_0$.

It is important to note that, in many cases, the period of time over which the approximation

$$V(x) \approx V_0 = \text{constant} \quad (24)$$

is valid can be comparable with the observation time (or even with the service life of the system). The reason is that corrosion is, generally speaking, a slow process and under real, practical conditions, values of the critical pit depth of the system, x_{cr} , (e.g., wall thickness of a pipe) and typical service life, t_s , impose significant restrictions on the values of the initial and average corrosion current densities and, thus, on the potential and concentration drops that might be observed in a corrosion cavity [20]. Thus, as follows from Faraday's law, if x_{cr} does not exceed the order of 1–10 mm, and if the order of t_s is not less than 1 year, the initial corrosion current densities in real pits cannot exceed values of 10^{-4} – 10^{-3} A/cm², with the understanding that the polarization curve (corrosion current density versus potential) does not change as the pit propagates [20]. Such low current densities can arise only from relatively low values of the potential and concentration drops in open pits. In particular, it is shown that if localized corrosion takes place in an electrolyte having a conductivity of the order of that of seawater, it is possible to neglect the potential drop in an open corrosion cavity and hence it is possible to regard the rate of pit propagation as being constant under constant environmental conditions. The same conclusion holds for the pitting of 316L stainless steel for practically any composition of the external electrolyte. This issue is discussed in greater depth in Ref. [20].

2.3. Rate of pit repassivation

As noted above, we assume that the repassivation process obeys a first-order decay law (see Eq. (8)). The repassivation constant, γ , is, in general, a function of the external conditions, including the corrosion potential, temperature, and electrolyte composition. Generally speaking, γ is also a function of the depth of the pit, x , because the local potential in the solution at the cavity surface depends on x , i.e. γ might be a function of both the spatial coordinates and time. Of course, if the potential and concentration drops inside the corrosion cavity are insignificant during pit propagation, it is possible to neglect changes in parameter γ (see above). In the current investigation, we assume, for simplicity, and hence to facilitate the development of analytical expressions for the damage functions f_a and f_p , that γ is a constant [1]. Of course, the value of this constant still depends on the external conditions, such as potential, pH, and concentration of aggressive species in the bulk electrolyte. However, we can imagine the situation when the potential and concentration drops inside the pit are significant and time-dependent (for example, in extremely dilute solutions or in closed pits); in which case the probability of repassivation will be a function of pit depth and hence pit age. It also can be that active pits cannot exist if the potential, E , at the pit internal surface is less than some critical value, E_{cr} . Accordingly, if the value of E_{cr} is reached at some pit depth, x_{cr} , active pits passivate and cannot penetrate further into the metal. Accordingly, Eq. (16) cannot be used.

3. Statistical properties of the damage function

In this section of the paper, we explore and develop the relationship that exists between deterministic and statistical methods for predicting the progression of corrosion damage. Our objective is to show mathematically that there exists a close correspondence between damage function analysis (DFA), which has been described at some length in the first part of this paper and extreme value statistics (EVS). The latter technique has been used extensively to extrapolate damage (maximum pit or crack depth) from small samples in the laboratory to larger area samples in the field. Furthermore, DFA provides a means of calculating the central and scale parameters and their time-dependencies in EVS from first principles and hence represents a unification of the two philosophies.

From the statistical point of view, all distributed properties of the system are completely determined by a cumulative distribution function (CDF), $\Phi(x)$. By definition, $\Phi(x)$ is the probability that the depth of a randomly selected pit is $\leq x$. We will postulate that the pit distribution on the metal surface is uniform. Accordingly, the total number of nucleated pit in the whole system is $SN(t)$, where S is the area of the system and, from the definition of the integral damage function, F , the number of pits that have the depth $\leq x$, is $S[N(t) - F(x, t)]$. Accordingly, by definition of probability we have

$$\Phi(x, t) = \frac{S[N(t) - F(x, t)]}{SN(t)} = 1 - \frac{F(x, t)}{N(t)} \quad (25)$$

We see that the cumulative distribution function for a given observation time, $\Phi(x, t)$, can be calculated if we know (can calculate) the integral damage function of the system (note that the number of nucleated stable pits, $N(t)$ simply equals $F(0, t)$). This relation can be regarded as being the bridge between the statistical and deterministic approaches for estimating the accumulation of localized corrosion damage on a surface.

Let us calculate, for example, the failure probability, P_f , of a system. By definition, P_f is the probability that at least one corrosion event in any form (pit, crevice, stress corrosion crack, or fatigue crack) reaches a depth, x , at a given observation time, t , where x , in this case, is the critical dimension. It is evident that the probability of a corrosion event not achieving the depth x at the time, t , is $\Phi(x, t)$. Accordingly, the probability that none of the corrosion events will reach the depth of x is, $\Phi(x, t)^{SN(t)}$ where S is the surface area of the system and, finally, the probability of failure is

$$P_f(x, t) = 1 - \{1 - F(x, t)/N(t)\}^{SN(t)} \quad (26)$$

Using the well known limit relation, $\lim(1 + a/x)^x \rightarrow \exp(a)$ as $x \rightarrow \infty$, and by assuming that $F(x, t)/N(t) \ll 1$ and $SN(t)$ is a large number, we can rewrite Eq. (26) in the form

$$P_f(x, t) = 1 - \exp\{-SF(x, t)\} \quad (27)$$

As has been shown experimentally, in many practical cases, the asymptotic behavior (for large values of x) of the CDF can be described by the exponential relationship [8,23].

$$\Phi(x, t) = 1 - \exp[-(x - u)/\alpha] \quad (28)$$

where u is the central parameter (the most frequent value) and α is the scale parameter, which defines the width of the distribution. Accordingly, as follows from Eq. (28), the extreme value distribution (EVD), $\Psi(x, t)$ (the probability that the largest value of pit depth $\leq x$) is described by a double exponent (Gumbel Type I extreme value distribution) in the form [22].

$$\Psi(x, t) = 1 - P_f = \exp[-\exp(-y)] \quad (29)$$

where

$$y = (x - h)/\alpha \quad (30)$$

and $h = u + \alpha \ln S$.

In many applications, the Type 1 distribution has been claimed to account for the statistical nature in the observed behavior of corrosion systems [8,9,21,23]. Specifically, the Type I extreme value distribution is used for extrapolating corrosion damage measured on a series of small samples of area, s , to a large system (for example, tanks or pipe lines) with area, S [24]. In this case, the probability of failure can be estimated from the relation

$$P_f(x, t) = 1 - \exp\{-\exp[-(d - [h + \alpha \ln(S/s)])/\alpha]\} \quad (31)$$

where d is the wall thickness and parameters h and α are measured by using the small samples.

It is interesting to determine whether damage function analysis (DFA) can predict the behavior of the extreme value distribution. For simplicity, we will consider the limiting, but real, case when the observation time is much longer than the induction time for the majority of nucleated stable pits (“instantaneous” nucleation conditions). Experimentally determined extreme value distributions for pits have been reported for these conditions [9]. In addition, we also assume that the pit propagation rate is so low that it can be considered to occur at a constant rate, V . Under these conditions, as follows from Eqs. (16), (17) and (25), the cumulative distribution function is given by

$$\Phi(x, t) = 1 - \exp(-\gamma x/V) U_+(t - x/V) \quad (32)$$

As noted by many sources [8,21], an important characteristic of the unlimited CDF (see Eq. (28)) is that it implies a small, but finite, probability of observing a pit of exceptional depth. The CDF given by Eq. (32) was obtained from a conservation law and naturally it is free from that weakness (there are no pits for $x > Vt$). For $x \leq Vt$ the CDF given by Eq. (32) coincides with the CDF described by Eq. (28), if we choose $\alpha = V/\gamma$ and $u = 0$, i.e. parameters α and u do not depend on time. However, experiment shows that parameters α and u are generally functions of time, and, particularly, the central parameter, u is positive [7–9]. Moreover, for short periods of time, we can neglect the repassivation of pits, i.e. let $\gamma = 0$ in Eq. (32). In this case, Eq. (32) reduces to a step function. However, experimentally observed extreme value distributions with $u > 0$ for systems where the period of time over which damage has developed is of order of 10^2 – 10^3 h [7], i.e. for periods that are much lower than the service life, t_s , of many practical systems, leaves little doubt that a distribution exists in the cavity growth rate, as alluded to earlier in this paper.

Because, under these limiting conditions, we neglect the nucleation stage of pit life (“instantaneous” nucleation) and because we also neglect the repassivation of pits, the only explanation of the inconsistency noted above must arise from the propagation of pits. In other words, Eq. (7) cannot be used, in the general case, for describing the flux density of pits. It has been tacitly assumed above that the rate of pit propagation is unequivocally determined by its depth and by the external conditions, i.e. there is no distribution in pit propagation rate for pits with equivalent depth. However, it is well known that the morphology of pits on any given surface can vary significantly, with some shapes favoring more rapid mass and charge transfer, and hence greater propagation rate [8]. In addition, some pits will initiate at metallurgical features that may favor more rapid propagation, e.g. MnS inclusion [8]. The distribution in pit propagation rate might also be explained, for example, by the spatial distribution in electrochemical activity of the anodic and cathodic sites on the corroding surface [7].

In this article, we will assume, for simplicity, that the pit propagation rate does not change significantly during the propagation stage. This assumption can be

justified for many real systems [20]. In generalizing DFA, for this case, we assume that the pits that propagate at a constant rate, v , nucleate in accordance with the equation.

$$n(t) = \int_0^{\infty} \lambda(t, v) dv \quad (33)$$

Here, the function $\lambda(t, v)$ yields the number of pits with propagation rates between v and $v + dv$, that nucleate in the period of time between t and $t + dt$ (per cm^2). For the total number of nucleated pits, we have by analogy

$$N(t) = \int_0^{\infty} A(t, v) dv \quad (34)$$

where $A(t, v)$ yields the total number of pits with propagation rates between v and $v + dv$ that are nucleated during the observation time, t , (per cm^2). Finally, it is evident that

$$A(t, v) = \int_0^t \lambda(\tau, v) d\tau \quad (35)$$

Eq. (7), for the flux density of active pits in the absence of the distribution in pit propagation rate, together with $V(x) \approx \text{constant}$, can be rewritten in the following form (see Eq. (12)):

$$j_a(x, t) = f_a(x, t)V(x) = \exp(-\gamma\theta)n(t - \theta) = \exp(-\gamma x/V)n(t - x/V) \quad (36)$$

and hence, when a distribution in the pit propagation rate is present, this expression can be generalized as

$$j_a(x, t) = \int_0^{\infty} \exp(-\gamma x/v)\lambda(t - x/v, v) dv \quad (37)$$

Under these conditions, the solutions of transport equation (3) have the form

$$f_a = \int_0^{\infty} \frac{\exp(-\gamma x/v)\lambda(t - x/v, v)}{v} dv \quad (38)$$

$$f_p = \int_0^{\infty} \frac{\gamma \exp(-\gamma x/v)A(t - x/v, v)}{v} dv \quad (39)$$

and

$$F = \int_0^{\infty} \exp(-\gamma x/v)A(t - x/v, v) dv \quad (40)$$

Let us assume that the distribution in pit propagation rate does not depend on time, i.e.

$$\lambda(t, v) = n(t)\psi(v) \quad (41)$$

and, correspondingly,

$$A(t, v) = N(t)\psi(v) \quad (42)$$

where the function, $\psi(v)$, satisfies the evident normalization condition

$$\int_0^{\infty} \psi(v) dv = 1 \quad (43)$$

Accordingly, we have for the integral damage function and the cumulative damage function the following expressions:

$$F(x, t) = \int_0^{\infty} N(t - x/v) \exp(-\gamma x/v) \psi(v) dv \quad (44)$$

and

$$\Phi(x, t) = 1 - \int_0^{\infty} N(t - x/v) \exp(-\gamma x/v) \psi(v) dv / N(t) \quad (45)$$

respectively. In particular, for the case of instantaneous nucleation, we have

$$\Phi(x, t) = 1 - \int_{x/V}^{\infty} \exp(-\gamma x/v) \psi(v) dv \quad (46)$$

To move further, we must assume a distribution function, $\psi(v)$, for the pit growth rate. For our purposes, it is most convenient to approximate $\psi(v)$, by Laplace's distribution function [25]

$$\psi(v) = \frac{\exp(-|v - V|/\beta)}{2\beta} \quad (47)$$

with the mean pit propagation rate, V , and dispersion $\sigma^2 = 2\beta^2$. Strictly speaking, distribution (47) satisfies the normalization condition $\int_{-\infty}^{\infty} \psi(v) dv = 1$, but not condition (43). The proper form of distribution (47) that satisfies conditions (43) is

$$\psi(v) = \frac{\exp(-|v - V|/\beta)}{2[\beta - \exp(-V/\beta)]} \quad (48)$$

However, for $V/\beta \geq 2$, distributions (47) and (48) practically coincide.

Generally, values for the kinetic parameters V and β (along with parameters that described pit nucleation and repassivation) can be found from independent experiments or might even be estimated from first principles. In any event, all unknown parameters can also be determined by fitting Eqs. (44) or (27) to the experimentally measured CDF or EVD functions, as is customary, by applying a purely statistical approach. However, the application of DFA for estimating localized corrosion damage has real advantages over the purely statistical approaches. Thus, DFA yields the connection between the CDF and the physical parameters that determine the accumulation of damage. This connection allows us to reduce the number of fitting parameters for the CDF, to predict the time dependencies of these parameters, and to predict the dependencies of some fitting parameters on the external conditions (corrosion potential, temperature, electrolyte composition, etc.).

As an example, let us consider the extrapolation of corrosion damage into the future for the system that has been investigated in Ref. [7]: corrosion of manganese steel in CO₂-acidified seawater. Fig. 2 shows experimental extreme value distributions for pit depth measured for six different times (from $t_1 = 336$ h to $t_6 = 1176$ h).

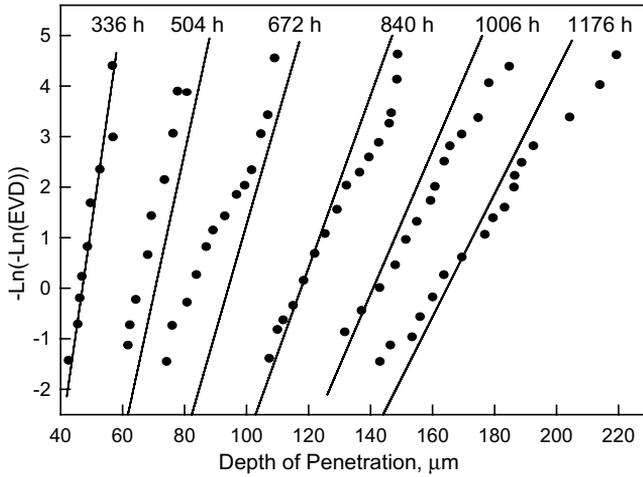


Fig. 2. Extreme value distribution functions (EVDs) versus exposure time for the pitting of manganese steel in CO₂-acidified seawater. Only the data for $t = 336$ h were used for fitting, in order to determine the central and scale parameters. Experimental data are taken from Fig. 5 in Ref. [7].

We will assume that we know nothing about the kinetic parameters for this system. Nevertheless, we will try to predict the propagation of the damage into the future by using only data obtained at $t = t_1$ and by using only the simplest, qualitative assumption concerning the damage propagation process.

First of all, we assume that the induction time for pit nucleation is much smaller than t_1 and, accordingly, that pit nucleation can be regarded as being instantaneous. This assumption is reasonable, if the environment is reasonably aggressive (high chloride concentration) and the exposure time is large, as is the case in this example. For example, many Fe–Cr alloys display pit induction times of the order of 10^2 s for commonly encountered environmental conditions [14]. We will also assume that t_1 is much smaller than the service life for normal structures made from this steel, and, accordingly, it is possible to neglect pit repassivation for $t \leq t_1$.

Substitution of Eq. (47) into Eq. (44) with $N(t) = N_0U_+(t)$ (instantaneous nucleation) and $\gamma = 0$ (no pit repassivation) yields:

$$F(x, t) = N_0 \left[1 - \frac{1}{2} \exp \left(\frac{x/t - V}{\beta} \right) \right] \quad \text{for } x \leq Vt \tag{49}$$

and

$$F(x, t) = \frac{N_0}{2} \exp \left(\frac{V - x/t}{\beta} \right) \quad \text{for } x > Vt \tag{50}$$

Because we are interested in the behavior of the CDF for large values of x , we obtain the following expression for the EVD:

$$\Psi(x, t) = 1 - P_f = \exp \left[-\frac{SN_0}{2} \exp \left(\frac{V - x/t}{\beta} \right) \right] \quad (51)$$

which absolutely coincides with the Type I extreme value distribution (Eqs. (29) and (30)) if we choose

$$\alpha = \beta t \quad \text{and} \quad h = [V + \beta \ln(0.5SN_0)]t \quad (52)$$

The reader will note that Eq. (51) does not contain parameters related to the nucleation of damage or to delayed repassivation, because we have assumed instantaneous nucleation conditions and we postulated that (for this particular case) delayed repassivation was not important. However, in the general case, both assumptions are invalid, and hence it is necessary to use Eq. (45) to derive the extreme value distribution function. These calculations can only be performed numerically, in the general case, and their use in deriving extreme value distribution functions will be illustrated in a subsequent paper.

Proceeding now with our analysis of the pitting of manganese steel in CO₂-acidified seawater, we see that fitting the scale parameter, α , and the central parameter, h , from Eqs. (29) and (30) to the experimental data for $t = 336$ h yields $\alpha = 3.7 \mu\text{m}$ and $h = 50 \mu\text{m}$. In accordance with Eq. (52), we have $\beta = 0.011 \mu\text{m/h}$ and $V + \beta \ln(0.5SN_0) = 0.15 \mu\text{m/h}$. Using these values for the parameters, we calculated EVDs for different times assuming that, even for $t_6 = 1176$ h, pit repassivation is not important. Satisfactory agreement between the experimental and predicted data is observed (Fig. 2).

DFA allows us to explore the influence of repassivation on the time-dependencies of parameters α and h . If the distribution in propagation rate is sufficiently sharp ($V \gg \beta$), Laplace's distribution can be considered to be an approximation of the δ -function. Under these conditions, for the case of instantaneous nucleation, we have from Eq. (44):

$$F(x, t) = N_0 \int_{x/V}^{\infty} \exp(-\gamma x/v) \psi(v) dv \approx N_0 \exp(-\gamma x/V) \int_{x/V}^{\infty} \psi(v) dv \quad (53)$$

By analogy with Eq. (52), it is easily shown that parameters α and h can be expressed as

$$\alpha = \frac{\beta t}{1 + \gamma \beta t/V}, \quad \text{and} \quad h = \frac{[V + \beta \ln(0.5SN_0)]t}{1 + \gamma \beta t/V} \quad (54)$$

We see that, for small values of t , the scale and central parameters can be described by Eq. (52), i.e. they are proportional to time. However, for large observation times, parameters α and h go to limits that are independent of time. This fact can be regarded as being physically evident, because at sufficiently large times all pits become passive (the damage function becomes “frozen”) and further propagation of damage cannot occur, provided that $\gamma > 0$. This conclusion concerning the achievement of limiting pitting depth also flows from a formal statistical treatment of the experimental data for underground pipelines made from carbon steels [4]. The “freezing”

of damage functions can also be seen in the propagation of corrosion damage on aluminum in tap water [9].

In the more general case, we suggest the following, simple expressions for representing the time dependencies of the scale and central parameters:

$$\alpha = \frac{\alpha_1 t}{1 + (\alpha_1/\alpha_\infty)t}, \quad \text{and} \quad h = \frac{h_1 t}{1 + (h_1/h_\infty)t} \quad (55)$$

For small times, Eqs. (55) yields the linear dependencies, $\alpha = \alpha_1 t$ and $h = h_1 t$, and for large times it yields the limiting values of $\alpha = \alpha_\infty$ and $h = h_\infty$. It is evident that experimental data for at least two times are required for determining the unknown parameters α_1 , h_1 , α_∞ and h_∞ . Fig. 3 shows that Eqs. (55) can be used for extrapolating experimental data from Ref. [9] for the pitting of aluminum in tap water to the future using Eq. (54) yields essentially the same results for this example. It is interesting to note that Finley [26] suggested that the experimental data for the pitting corrosion of aluminum in tap water (from Ref. [9]) could be described by assuming that α does not change with time and that h could be described by the logarithmic relation

$$h = b \ln(t) + c \quad (56)$$

However, it is evident that Eq. (56) cannot describe the experimental data for small values of t , when the condition $h \rightarrow 0$ for $t \rightarrow 0$ must be fulfilled, and for large values of t when h must go to a constant value. It should be emphasized that the power law (see Ref. [3]) cannot describe the cessation of localized corrosion damage due to pit passivation. That is why, in our opinion, it is much more appropriate to use a hyperbolic law than to employ a logarithmic law (and power law) for representing the time dependencies of the EVS parameters.

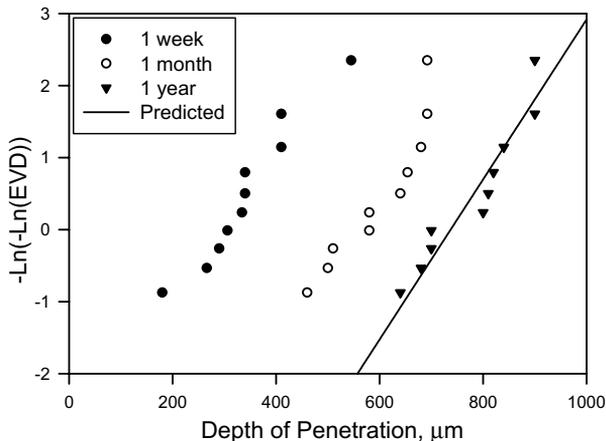


Fig. 3. Extreme value distribution functions (EVDs) versus exposure time for the pitting of aluminum in tap water [9]. Only the data for $t = 1$ week and 1 month were used for fitting, in order to determine the central and scale parameters. Experimental data are taken from Table 3, Ref. [9].

It is important to note that the Gumbel asymptotic extreme (Type I) can be used for describing the statistics of localized corrosion damage when repassivation (death) is considered, even though nucleation is instantaneous (Fig. 4) or even for the case of progressive nucleation where two different nucleation functions have been considered (Figs. 5 and 6). Note that Fig. 5 shows the EVD for the nucleation rate function for the deterministic point defect model. Numerical calculation shows that, in all of

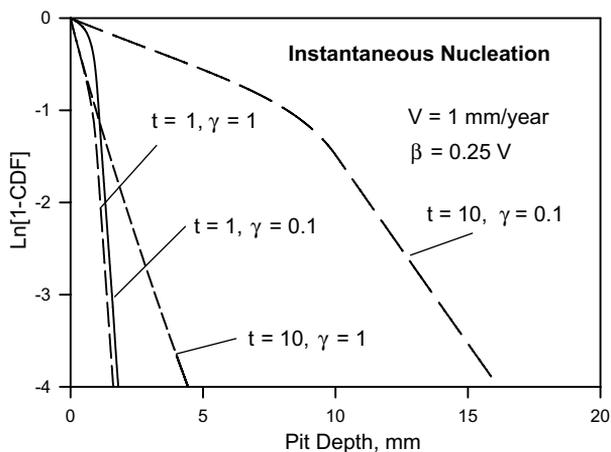


Fig. 4. Variation of the cumulative distribution function (CDF) with pit depth as a function of time for instantaneous nucleation. Observation times, t , are measured in years and the delayed repassivation constant, γ , is given in units of year^{-1} .

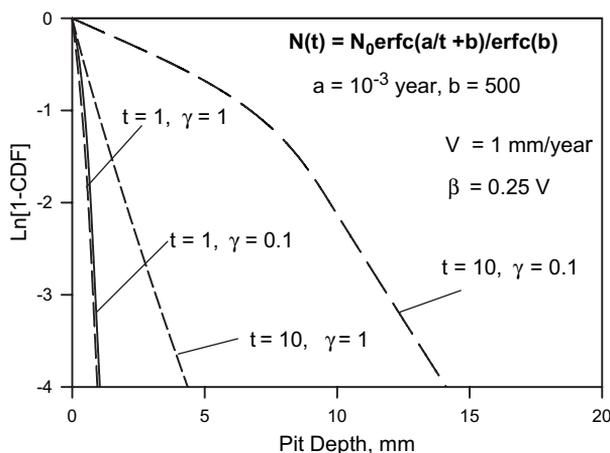


Fig. 5. Variation of the cumulative distribution function (CDF) with pit depth as a function of time for the case when the nucleation of pits is described by the point defect model. Observation times, t , are measured in years and the delayed repassivation constant, γ , is given in units of year^{-1} .

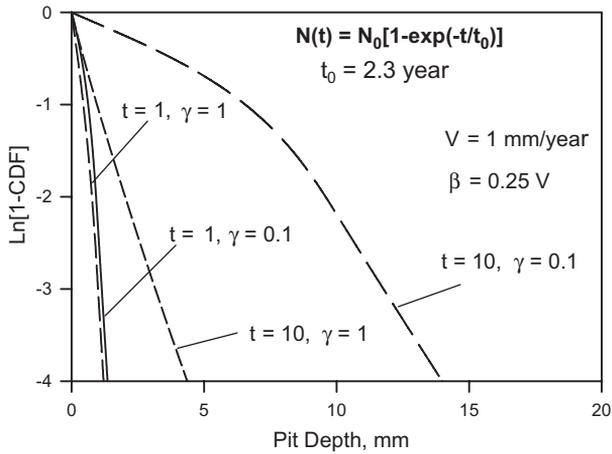


Fig. 6. Variation of the cumulative distribution function (CDF) with pit depth as a function of time for the case when the nucleation of pits is described by an exponential function. Observation times, t , are measured in years and the delayed repassivation constant, γ , is given in units of year^{-1} .

these cases, the dependencies of $\ln(1 - \text{CDF})$ on pit depth, x , can be approximated by straight lines, at least for sufficiently large values of x . The work presented in this paper, therefore, provides a theoretical basis for applying Type I extreme value distributions for real corrosion systems.

4. Summary and conclusions

In this article, a new, general method for calculating damage functions has been described. The method is based on the analogy of the propagation of corrosion pits and the movement of particles. In principle, it can be applied for describing damage propagation in arbitrarily complicated systems in the presence of different kinds of localized corrosion events, including crevice corrosion, stress corrosion cracking, and corrosion fatigue. The method can be applied when the external conditions (corrosion potential, temperature, electrolyte composition, etc.) change with time. In particular, generalization of the point defect model for the case of variable external conditions has been achieved.

On the basis of damage function analysis, a method for extrapolating experimentally measured corrosion damage to the future, within the realm of extreme value statistics (EVS), has been developed. This method can be used under conditions when not all, or even none, of the kinetic parameters that determine the pit nucleation rate, pit propagation rate, and pit repassivation rate, are known. The unknown parameters are determined by comparing results of analytical or numerical calculation of integral damage functions or extreme value distribution functions with the experimentally observed functions for short-term experiments (usually it is much

more easy to measure EVD functions than IDF's). After determining values for the unknown parameters, damage functions for long-term exposure are predicted. Of course, the values of the unknown parameters and the quality of prediction can be improved by updating the parameter values at each scheduled inspection.

Combining DFA and the results of periodic inspections has significant advantages over a purely statistical approach, as noted previously. Thus, as has been shown above, DFA allows us to express the fitting parameters for the extreme value distribution in terms of the values for physical parameters in the deterministic models contained within DFA (e.g. pit nucleation and propagation rates, repassivation constants, etc.) or in terms of parameter values determined from independent experiments. Accordingly, it is possible to find appropriate forms for the time-dependencies of empirical coefficients for traditional, statistical analysis. Moreover, it becomes possible to predict the changes of the statistical fitting parameters contained within the extreme value distribution with variations in the external conditions (corrosion potential, temperature, bulk composition of the electrolyte), because the connections between the statistical and physical parameters has been established.

Acknowledgements

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Appendix A

This appendix describes the generalization of point defect model (PDM) for passivity breakdown for the case where the external conditions vary with time.

In the original version of PDM [13–17], the pit nucleation rate was obtained from the criterion for pit initiation:

$$(J_{ca} - J_m) \times (t - \tau) \geq \xi \quad (\text{A.1})$$

where J_{ca} is the cation vacancy flux in the barrier layer of the passive film at the metal/barrier layer interface, J_m is the rate of annihilation of the cation or metal vacancies at the same location, t is the observation time, τ is the time of dissolution of the pit cap until rupture, and ξ is the critical “areal” concentration ($\#/cm^2$) of condensed vacancies that are required for the separation of the barrier layer from the substrate metal. This latter parameter can be obtained from the potential sweep rate dependence of the apparent breakdown potential and can also be calculated from structural arguments [27,28]. However, Criterion (A.1) is valid only if all external

parameters (temperature, electrolyte composition, pH, corrosion potential, etc.) do not depend on time, and, accordingly, J_{ca} , J_m , and ξ are constants. In the general case, when the external conditions are time-dependent, instead of Criterion (A.1) we must use the following criterion:

$$\int_{t_0}^t [J_{ca}(t') - J_m(t')] dt' \geq \xi(t) \quad (\text{A.2})$$

Note that ξ corresponds to the number of cation vacancies per unit area condensed on the cation sub-lattice on the film side of the metal/barrier layer interface or the number of metal vacancies condensed on the metal lattice on the metal side of the interface, depending upon whether vacancy condensation occurs on the cation sub-lattice of the film or on the metal lattice, respectively. In any event, the value of ξ is of the order of $(2-3) \times 10^{15} \text{ cm}^{-2}$, depending upon the crystallographic faces involved [27,28]. The principal time-dependence of ξ most likely arises from expansion/contraction of the lattice as the temperature changes, in which case $\xi = \xi_0 \exp[-2\hat{\alpha}(T - T_0)]$, where $\hat{\alpha}$ is the coefficient of linear thermal expansion, T is the Kelvin temperature, T_0 is the reference temperature, and ξ_0 is the critical vacancy concentration at T_0 . For example, we evaluate $\exp[-2\hat{\alpha}(T - T_0)]$ for nickel (a simple, ccp metal with $\hat{\alpha} = 1.3 \times 10^{-5} \text{ K}^{-1}$ [29]) to be 0.9981 for $T = 373.15 \text{ K}$ (100 °C) and $T_0 = 298.15 \text{ K}$ (25 °C), assuming that vacancy condensation occurs on the metal lattice, from which we conclude that ξ can be considered to be quasi-constant. However, this may not be the case for passivity breakdown on a liquid metal, such as gallium [30], because of the much larger coefficient of expansion.

In previous work [27,28], J_m has been estimated from $J_m \leq i_{\text{passive}}^c/nF$, where i_{passive}^c is the steady-state passive current density at the point of film breakdown, n is the number of electrons involved in the annihilation reaction, and F is Faraday's constant. The inequality arises, because not all of the current may be carried by cation vacancies; indeed, in n-type passive films, such as those that form on iron and aluminum, where the principal point defects are either oxygen vacancies or metal interstitials, or both, the current density due to the flux of cation vacancies might be only a small fraction of the total current density. If the transport number of the cation vacancy (t_{cv}) in the barrier layer is known by independent experiment, then the value of J_m can be established precisely as $J_m = t_{cv}i_{\text{passive}}^c/nF$, where i_{passive}^c is the passive current density at the point of breakdown in the absence of a redox couple in the solution. In any event, methods have been developed for determining the rate of annihilation cation vacancies at the metal/barrier layer interface, primarily by analyzing electrochemical impedance data [31], so that J_m may be determined by independent experiment for any given set of external conditions. This leaves only J_{ca} in Eq. (A.2) to be determined by independent experiment, in order to affect a completely deterministic prediction of metastable pit nucleation rate. The rate constant for cation vacancy generation at the barrier layer/solution interface is readily determined using EIS and, for nickel, is found to be of the form $k = k_0 + A[\text{Cl}^-]^p$ [17], where k_0 is the rate constant for chloride free solutions and A and p are constants. For nickel in NaCl solutions [31], we have recently determined that $p = 1$;

that is, cation vacancy generation at the barrier layer/solution interface for passive nickel is first order in chloride concentration, a finding that is consistent with the point defect model.

On any real surface, a large number of potential breakdown sites exist corresponding to a distribution in the properties of the “weak spots”. Thus, examination of data reported by Shibata [32] and Fratesi [33], among others, suggests that the breakdown voltage is nearly normally distributed. The PDM assumes that the breakdown sites with respect to the distribution of diffusivity of cation vacancies is described approximately by a normal distribution function [17], i.e.

$$\frac{dN(D)}{dD} = -A \exp \left[-\frac{(D - \bar{D})^2}{2\sigma_D^2} \right] \quad (\text{A.3})$$

Here, $N(D)$ is the number of breakdown sites (per cm^2) that have diffusivities larger than D , and \bar{D} and σ_D are the average value and the standard deviation, respectively, of the diffusivity for the population of the breakdown sites. The negative sign in Eq. (A.3) means that $N(D)$ decreases with increasing D . Parameter A does not depend on D , so that normalization of the diffusivity distribution using the condition $N(0) = N_{\text{tot}}$, where N_{tot} is the total number of breakdown sites (per cm^2), yields

$$N(D) = N_{\text{tot}} \operatorname{erfc} \left(\frac{D - \bar{D}}{\sqrt{2}\sigma_D} \right) / \operatorname{erfc} \left(-\frac{\bar{D}}{\sqrt{2}\sigma_D} \right) \quad (\text{A.4})$$

The cation vacancy flux density, J_{ca} , is proportional to the diffusion coefficient of vacancies, D , i.e.

$$J_{\text{ca}} = DB \quad (\text{A.5})$$

where the function B depends on the on the external conditions (applied voltage, V_{app} , temperature, T , chloride activity, a_x , etc.). Thus, for the case of passivity breakdown in chloride solutions, the PDM yields:

$$B = \hat{a}u^{-\chi/2} \exp \left(\frac{\chi F \alpha V_{\text{app}}}{2RT} \right) a_x^{\chi/2} \quad (\text{A.6})$$

where α is the polarizability of the film/solution interface (i.e., dependence of the potential drop across the barrier layer/solution interface on the applied potential), χ is the cation oxidation state in the barrier layer, R is the gas constant, and F is Faraday's constant. In turn, parameters \hat{a} and u are defined as [13]

$$\hat{a} = \chi(F\varepsilon/RT)[N_A/\Omega]^{1+\chi/2} \exp(-\Delta G_S^0/RT) \quad (\text{A.7})$$

and

$$u = \frac{N_A}{\Omega} \exp \left(\frac{\Delta G_A^0 - \beta F p H - F \phi_{\text{f/s}}^0}{RT} \right) \quad (\text{A.8})$$

where ε is the field strength in the film, Ω is the mole volume per cation, ΔG_S^0 is the change of Gibbs energy for the Schottky-pair reaction ($\text{Null} \rightarrow V_M' + (x/2)V_O''$), assuming that this is the cation vacancy generation process—see Ref. [20], β is the

dependence of the potential drop across the film/solution interface on pH, $\phi_{f/s}^0$ is a constant (potential drop at the film/solution interface for $V_{app} = 0$, and pH = 0), and ΔG_A^0 is the standard Gibbs energy change for the chloride absorption reaction $V_O^{\bullet\bullet} + Cl_{aq}^- \rightleftharpoons Cl_O^\bullet$ ($V_O^{\bullet\bullet}$ is an oxygen vacancy in the film and Cl_O^\bullet is a chloride anion occupying a surface oxygen lattice site). A detailed discussion of these parameters is available in the original papers [13–17]. The assumption of a normal distribution of the breakdown sites with respect to D results in a near-normal distribution in the breakdown voltage and a left-acute distribution in the induction time, in agreement with experiment [14–17].

Let us denote by D_0 the diffusivity of a cation vacancy at temperature T_0 . We can calculate D at any other temperature by using the relation

$$D = D_0 \omega \quad (\text{A.9})$$

where

$$\omega = \exp \left[-\frac{E_D}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (\text{A.10})$$

and E_D is the energy of activation for diffusion.

Substituting Eqs. (A.5) and (A.9) into Eq. (A.2) yields the following criterion for metastable pit nucleation as:

$$D_0 \geq D_{cr}(t) = \frac{\xi + \int_{\tau}^t J_m(t') dt'}{\int_{\tau}^t \omega B(t') dt'} \quad (\text{A.11})$$

This criterion has to be understood in the following way. Let us assume that, at $t = 0$ (at the beginning of corrosive attack), a potential breakdown site is characterized by a cation vacancy diffusivity of D_0 . Criterion (A.11) states that the nucleation of metastable pits occurs within the observation time, t , on those and only on those sites that have $D_0 \geq D_{cr}(t)$.

Substitution of Eq. (A.9) into Eq. (A.4) yields an expression for the number of metastable pits (per cm^2) that nucleate during the period of time $(0, t)$.

$$N(t)_{MP} = N_{tot} \operatorname{erfc} \left(\frac{D_{cr}(t) - \bar{D}_0}{\sqrt{2}\sigma_{D_0}} \right) / \operatorname{erfc} \left(-\frac{\bar{D}_0}{\sqrt{2}\sigma_{D_0}} \right) \quad (\text{A.12})$$

Subscript “0” in Eq. (A.12) means that the values are calculated at temperature T_0 , i.e. at $t = 0$. Under constant external conditions, Eq. (31) reduces to the previously developed expression [5]

$$N(t)_{MP} = N_{tot} \operatorname{erfc} \left(\frac{a}{t - \tau} + b \right) / \operatorname{erfc}(b) \quad (\text{A.13})$$

where $a = \xi / (B\sqrt{2}\sigma_{D_0})$ and $b = (J_m/B - \bar{D}) / (\sqrt{2}\sigma_{D_0})$.

By differentiating Eq. (A.13), we obtain an expression for calculating the rate of nucleation of metastable pits:

$$n_{\text{MP}} = \frac{dN_{\text{MP}}(t)}{dt} = \frac{\sqrt{2}}{\text{erfc}(-\bar{D}_0/\sqrt{2}\sigma_{\text{D}_0})\sqrt{\pi}\sigma_{\text{D}_0}} \exp\left[-\frac{(D_{\text{cr}}(t) - \bar{D}_0)^2}{2\sigma_{\text{D}_0}^2}\right] \frac{dD_{\text{cr}}(t)}{dt} \quad (\text{A.14})$$

where, in accordance with Eq. (A.11),

$$\frac{dD_{\text{cr}}(t)}{dt} = \frac{d\xi/dt + J_{\text{m}}(t)}{\int_{\tau}^t \omega B(t') dt'} - \frac{\omega B(t)(\xi(t) + \int_{\tau}^t J_{\text{m}}(t') dt')}{[\int_{\tau}^t \omega B(t') dt']^2} \quad (\text{A.15})$$

For the case when the external conditions do not depend on time, we have a more simple expression

$$n_{\text{MP}} = \frac{N_{\text{tot}}2a}{\text{erfc}(b)\sqrt{\pi}} \frac{\exp\left[-\left(\frac{a}{t-\tau} + b\right)^2\right]}{(t-\tau)^2} \quad (\text{A.16})$$

which we previously derived [5].

It is important to note that all expressions for N_{MP} or n_{MP} are valid only for $t > \tau$. If $t \leq \tau$, we simply have $N_{\text{MP}} = 0$ and $n_{\text{MP}} = 0$. However, for the majority of cases, the observation time, t , is much greater than τ , and accordingly it is possible to let $\tau \approx 0$. Under these conditions, Eqs. (A.13) and (19) yield Eq. (20) (assuming that $N_0 = \zeta N_{\text{tot}}$), which has been previously used for estimating the number of stable pits nucleated under constant external conditions.

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