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Deterministic Prediction of Localized Corrosion Damage

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The accumulation of damage due to localized corrosion [pitting, stress corrosion cracking (SCC), corrosion fatigue (CF), crevice corrosion (CC), and erosion-corrosion (EC)] in complex industrial systems, such as power plants, refineries, desalination systems, etc., poses a threat to continued safe and economic operation, primarily because of the sudden, catastrophic nature of the resulting failures. Of particular interest in managing these forms of damage is the development of robust algorithms that can be used to predict the integrated damage as a function of time and as a function of the operating conditions of the system. Because complex systems of the same design rapidly become unique, due to differences in operating histories, and because failures are rare events, there is generally insufficient data on any given system to derive reliable empirical models that capture the impact of all (or even some) of the important independent variables. Accordingly, the models should be, to the greatest extent possible, deterministic with the output being constrained by the natural laws. In this paper, I outline the theory of the initiation of damage, in the form of pitting on aluminum in chloride solution, and then describe the deterministic prediction of the accumulation of damage from SCC in Type 304 SS components in the primary coolant circuits of Boiling Water (Nuclear) Reactors (BWRs. These cases have been selected to illustrate the various phases through which localized corrosion damage occurs.

Keywords *: deterministic, prediction, corrosion damage, pitting, stress corrosion cracking*

1. Introduction

Over the past decade, we have developed powerful, deterministic models and algorithms for predicting the accumulation of damage due to localized corrosion, including pitting, stress corrosion cracking (SCC), crevice corrosion (CC), and corrosion fatigue (CF) in complex industrial systems. Systems that have been modeled to date include electrical power generating facilities,[1-8] among others. These models and algorithms are "deterministic", because their predictions are constrained by the relevant natural laws. Because corrosion is essentially an electrochemical phenomenon, the primary constraints are the conservation of charge and Faraday's Law. The advantage of determinism, as opposed to empiricism, is that deterministic models require minimal calibration (for example, a single crack growth rate for a given set of environmental and mechanical conditions, in the case of SCC). Accordingly, deterministic models may be used to predict damage in systems that are unique (as are all industrial systems, once they have operated for any significant time), for which failure databases do not exist. The "coupled environment" models [coupled environment pitting model (CEPM), coupled environment crevice model (CECM), coupled environment fracture model (CEFM), and the coupled environment corrosion fatigue model (CECFM)] that have been used in this work are, to our knowledge, the only currently available deterministic models for predicting the evolution of damage due to localized corrosion.[2-4),9-15] Furthermore, when coupled with the point defect model (PDM) for passivity breakdown, and hence for the nucleation of damage, the resulting algorithms provide a comprehensive theoretical basis for predicting localized corrosion damage.[14-16] The algorithms have been used to predict damage due to stress corrosion cracking in BWRs (the DAMAGE-PREDICTOR and ALERT codes, eleven reactors being modeled to date),[1] pitting damage in condensing heat exchangers,[2] and pitting/SCC in LP steam turbine disks.[3]

The development of effective localized corrosion damage prediction technologies is not only essential for the successful avoidance of unscheduled downtime, but it is vital 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. The present author has argued that this strategy is inaccurate and inefficient, and that in many instances it is too conservative.[17] Instead, I suggest that damage function analysis (DFA)[14),16-18)] is a more effective method for predicting the progression of damage, particularly when combined with periodic inspection. Although corrosion is generally complicated mechanistically, a high level of determinism has been achieved in various treatments of both general and localized corrosion, and the resulting deterministic models can be used to predict accumulated damage in the absence of large calibrating databases.

In this paper, the foundations of the deterministic predictions of damage due to localized corrosion are outlined. The application of damage function analysis (DFA) is illustrated with reference to the pitting of aluminum in chloride-containing solutions and to the accumulation of damage due to stress corrosion cracking (SCC) in water-cooled nuclear power reactors.

2. Nucleation of localized corrosion damage

All localized corrosion on passive metals and alloys (e.g., stainless steels) begins with passivity breakdown. Accordingly, any viable, mechanistically based model for the initiation of localized corrosion must address that issue. A commonly observed scenario is that stress corrosion and corrosion fatigue cracks nucleate from pits, so that any viable theoretical treatment for the accumulation of localized corrosion damage on a surface must begin by addressing not only passivity breakdown but also the transition from metastable pitting to stable pitting, pit growth, and the transition of a pit into a crack. This must be done while recognizing that the nucleation of damage is a progressive phenomenon, in that new damage nucleates while existing damage grows and dies. The theory that has been developed to account for the nucleation of localized corrosion damage forms the basis of damage function analysis (DFA),[16-18)] which has now been developed to the point where damage due to pitting, SCC, and CF may be predicted with considerable accuracy in actual industrial systems.[2,3)] Space does not allow a comprehensive discussion of all aspects of the theory of initiation here, so only a brief outline will be given.

The point defect model (PDM)[14,18)] for the growth and breakdown of passive films attributes passivity breakdown at a single site on a surface to the condensation of cation vacancies at the metal/film interface. This process is postulated to occur at a structural inhomogeneity within the barrier layer of the passive film (e.g. at the edge of an inclusion), which is characterized by high cation vacancy diffusivity and/or by a high cation vacancy concentration. Condensation occurs because some environmental stress (e.g. the absorption of chloride ions into surface oxygen vacancies) results in the generation of cation vacancies at the film/solution (f/s) interface and hence in an enhanced flux of cation vacancies across the barrier layer from the (f/s) interface to the metal/film (m/f) interface. If the flux is sufficiently high that all of the vacancies arriving at the m/f interface cannot be annihilated by cation injection from the underlying metal, the excess vacancies condense to form a void. The void represents a local separation of the barrier layer from the underlying metal, so that the barrier layer ceases to grow into the metal while dissolution at the f/s interface continues to occur. However, growth of the barrier layer into the metal continues to take place at the surrounding areas, where detachment of the film has not occurred, at a rate in the steady state that matches the film dissolution rate. Accordingly, the film over the cation vacancy condensate thins and eventually ruptures to mark a passivity breakdown event. The resulting pit nucleus may repassivate "promptly" due to its failure to achieve the required separation between the local anode (in the forming cavity) and the local cathode (on the external surface), as demanded by the differential aeration hypothesis. If prompt repassivation occurs, the event is termed "metastable", and is detected as a current pulse in the external circuit when the system is under potential control. If the nucleus survives, by establishing the required anode/cathode separation, it exists as a stable pit, which will continue to grow until it dies due to "delayed" repassivation. One reason that has been postulated[18)] for delayed repassivation is the inability of a pit to obtain the necessary resources (oxygen reduction) from the external surfaces to meet the growth demands. This may happen either because of an inherent limitation in the rate of oxygen reduction or because neighboring pits compete for the same resources. This latter scenario results in the "survival of the fittest", and hence is Darwinian in nature.[18)] One inescapable result of delayed repassivation is that eventually all pits must die.

On any real surface, there exists a distribution in potential breakdown sites. In the present version of the PDM,[14-18)] it is assumed that the sites are normally distributed with respect to the cation vacancy diffusivity. That assumption leads to an analytical expression for the metastable pit nucleation rate at an observation time of τ as[16)]

$$n(\tau) = A\frac{exp\left[-\left(\frac{a}{\tau}+b\right)^2\right]}{\tau^2} \quad (1)$$

where

$$a = \frac{\xi}{\sqrt{2}\sigma_D B} \quad (2)$$

$$b = \frac{J_m}{\sqrt{2}\sigma_D B} - \frac{\overline{D}}{\sqrt{2}\sigma_D} \quad (3)$$

and

$$B = \frac{\chi F \varepsilon N_A a_x^{\chi/2}}{\Omega RT} \exp\left(\frac{\chi F(\beta.pH + \alpha.E_{corr}) + 2w}{2RT}\right) \quad (4)$$

The parameter ax is the activity of the aggressive ion (e.g. Cl^-) that adsorbs into a surface oxygen vacancy, α is the polarizability of the f/s interface, and β is the dependence of the potential drop across the f/s interface upon pH. $\overline{D}$ is the mean cation vacancy diffusivity, σ_D is the standard deviation in D, ξ is the critical (areal) concentration of cation vacancies in the condensate ($\xi \sim 3x10^{15}$ /cm^2), and Ω is the mole volume of the barrier layer per cation. The parameter J_m is the rate of annihilation of the cation vacancies at the m/f interface, where the film is attached, x is the barrier layer stoichiometry ($MO_{x/2}$), ε is the electric field strength within the film, and F is Faraday's constant. The quantity N_A is Avogadro's number, R is the gas constant, and T is the Kelvin temperature. The parameter w is an energy term related to absorption of aggressive anions into oxygen vacancies at the film/solution interface and the subsequent generation of cation vacancies. All of the parameters contained in Equations (1) to (4) can be measured, with the exception of w, either directly or indirectly. In the case of w, the value must be determined by calibration.

Parameter A in Eq. 1 is determined by normalization with respect to the finite density of potential breakdown sites on the surface. This quantity does not depend upon the time (. Accordingly, normalization of the nucleated pit population using the condition

$$N(\infty) = \int_o^\infty n(\tau)d\tau = N_0 \quad (5)$$

requires that

$$A = N_0 / \int_o^\infty \frac{exp\left[-\left(\frac{a}{\tau}+b\right)^2\right]}{\tau^2} d\tau = \frac{N_0 2a}{\sqrt{\pi}\, erfc(b)} \quad (6)$$

N_0 is the maximum number density of breakdown sites (per cm^2) that can exist on the metal surface (regardless of whether metastable or stable pitting occurs) and erfc(x) is the complementary error function. Accordingly, the metastable pit nucleation rate per unit area of the surface becomes[16]

$$N(\tau) = \frac{N_0}{erfc(b)} erfc\left(\frac{a}{\tau}+b\right) \quad (7)$$

Only stable pits can act as sites for the nucleation of cracks, because the cavity must be sufficiently deep for the stress intensity factor to exceed the critical value for crack nucleation (K_{ISCC} and ΔK_{th} for SCC and CF, respectively). Accordingly, we must modify the above theory to calculate the rate of nucleation of stable pits as

$$N_{sp} = \lambda . N_{MS} \quad (8)$$

where λ is the probability that a breakdown event will survive prompt repassivation to form a stable pit. The theory for calculating λ from first principles is currently being developed. However, experiment shows that for stainless steels in chloride containing solutions at ambient temperature, λ has a value of about 10^{-4}; that is only about one in ten thousand breakdown events survives to become a stable pit. Of course, those that survive prompt repassivation are subject to delayed repassivation, so that a pit that grows to a size that can nucleate a crack is, indeed, a rare event.

By combining Equation (8) with a pit growth model, and by assuming that delayed repassivation is a first order process that is characterized by a decay constant γ, it is a relatively straightforward task to calculate the damage function (DF). The DF is the histogram of (stable) pit density on the surface versus pit depth in preselected increments. The value of the DF is that it corresponds to the measured pit depth distribution, and hence represents a vital link between experiment and theory. In order to illustrate some of the properties of the DF, we plot in Fig. 1 three predicted damage functions for different values of the delayed repassivation constant, γ. The quantity plotted on the ordinate is $\Delta F(L_1, L_2)/N_{o\lambda}$, where $\Delta F(L_1, L_2)$ is the number of pits having depths between L_1 and L_2 per unit area for a given observation time. The DFs shown in Fig. 1 were actually calculated for aluminum under the conditions given in the caption, and while they will differ from those predicted for stainless steels in power plant coolant circuits they provide a basis for exploring a number of important properties. Thus, for

the parameter values chosen, nucleation occurs "instantaneously"; that is, all of the pits nucleate within the first time increment. In the absence of delayed repassivation (γ = 0), all of the pits grow in unison and the DF takes the form of a single vertical bar.

However, when delayed repassivation occurs, pits die at various times that are less than the observation time and hence populate depths that are less than the maximum depth. Thus, for γ = 3 year^{-1}, only a small number of pits are still alive after an observation time of one year. In the case of more intense repassivation (γ = 5 year^{-1}), essentially all pits are predicted to be dead. Damage functions of the type shown in Fig. 1 have been calculated for different observation times, chloride concentrations, temperatures, and oxygen concentrations (and hence E_{corr}). As expected, each of these independent variables has an important impact on the depth of the predicted damage and on its distribution. For example, reducing [Cl^-] or E_{corr} induces a transition from instantaneous nucleation to progressive nucleation, where new damage nucleates while existing pits grow and die. This, too, has a profound impact on the form of the DF.

Another important advantage of damage function analysis (DFA) is that the DF expresses the "integral damage" (i.e., the penetration depth for a given observation time), and hence leads to a natural definition of failure. Thus, with reference to Fig. 1, no failure would have occurred if the critical dimension (h_{crit}, e.g. thickness of a steam generator tube) was 0.15 cm, but failure would have occurred if h_{crit} = 0.1 cm. In the present discussion, we are particularly interested in defining the critical dimension for the nucleation of stress corrosion and corrosion fatigue cracks.

According to Chen, et. al.,[19] two conditions must be satisfied for crack nucleation to take place; namely, $K_I > K_{ISCC}$ (for SCC) or $\Delta K_I > \Delta K_{I,th}$ (CF) and $(dL/dt)_{crack\ growth} > (dL/dt)_{pit\ growth}$. The first requirement defines the mechanical (fracture mechanics) condition that must be met for the prevailing stress and geometry while the second simply says that the nucleating crack must be able to "out run" the pit. Thus, we may define the critical pit depth for the nucleation of a crack as

$$h_{crit} = \left(\frac{K_{ISCC}}{A' \sigma} \right)^2 \qquad (9)$$

where σ is the stress and A' is a geometry dependent parameter that also incorporates short crevice factors. An equivalent expression can be written for the nucleation of a corrosion fatigue crack. Note that Eq[9] is a necessary, but not a sufficient, condition, because the velocity con

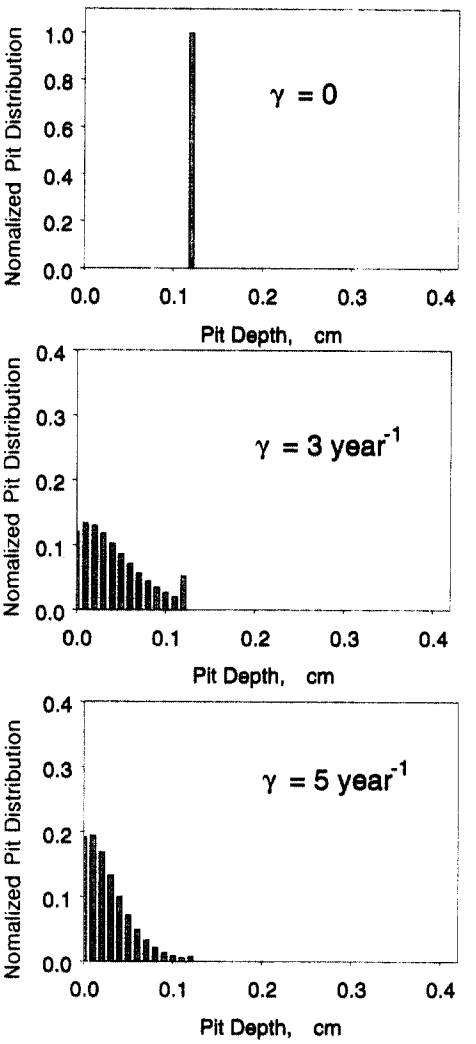

Fig. 1. Influence of the value of γ on normalized pit distribution for C_{NaCl} = 0.1 mol/L, E_{corr} = -0. 384 V (SHE), $_{pH}$ = 7, T = 25°C, and t_{obs} = 1 year.

straint must also be satisfied. Comparison of h_{crit} with the DF provides a measure of the probability that a pit exists on the surface of sufficient depth to satisfy the fracture mechanics condition. Alternatively, by calculating the DF for different observation times, it is possible to determine that time at which Eq[9] is satisfied to a preselected level of probability. The resulting time is termed the *crack initiation time*. Note that the DF provides a *probability* that a super critical pit will exist. In order to determine whether a super critical pit *actually* exists, it is necessary to multiply the probability given by the DF by the number of potential breakdown sites and by the survival probability. Clearly, the resulting product must be greater than one (pits can exist only as integers).

The concept of *integral damage* introduced above

through the damage function is exceedingly important in any discussion of the prediction of corrosion damage. This is because the "integral damage" is determined by integrating over the prior history, within which conditions may have changed at various times. This feature has not yet been incorporated into DFA, but it has been included in our predictions of accumulated damage in BWR primary coolant circuits from pre-existing cracks, as discussed below.

3. Integral(accumulated) damage and life time assessment

In the first case that we will discuss, it is assumed that a crack already exists in the structure and that the initial crack length is known by inspection. This is a common scenario, because most system operators perform inspections during scheduled outages. To use the inspection data effectively, it is necessary to extrapolate the damage to the next inspection time, taking into account the expected operating conditions. Extrapolation has been performed, in the past, mostly upon the basis of fracture mechanics models and techniques, which incorporate environmental data only inadvertently. However, the increasing demand for higher availability has led to the development of various radiolysis models for calculating the concentrations of electroactive species, such as H_2, O_2, and H_2O_2, as functions of the reactor operating parameters and the concentration of hydrogen added to the feedwater.[4-7),20-22)] One such model, ALERT, combines deterministic water chemistry and corrosion models for calculating radiolytic species concentrations in the HTCs of BWRs and for predicting the damage that accumulates from the corrosion processes (SCC).[1),4-7),9-13)] Because some of the radiolysis species are electroactive, they are instrumental in establishing the electrochemical corrosion potential (ECP) of components within the HTC.[1),4-7),13),24)] Extensive work in many laboratories worldwide has established that sensitized Type 304SS becomes increasingly susceptible to intergranular stress corrosion cracking in high temperature aqueous solutions as the ECP is increased above a critical value.[23)] Constant extension rate tests (CERTs), using round tensile specimens in actual BWR coolant at 288℃,[24)] has led the Nuclear Regulatory Commission (NRC) to adopt a value for the critical ECP (E_{crit}) of -0.23 V (SHE). However, we note that critical potentials as negative as -0.4V (SHE) have been observed in laboratory studies.[23)] A distribution in E_{crit} in an operating reactor is expected, because of the variability in the degree of sensitization (DOS) of the steel at welds and because of differences in neutron fluence experienced by in-vessel components. Because SCC occurs only when $ECP>E_{crit}$,[23)] the goal of any water chemistry control protocol for inhibiting cracking in BWR coolant circuits is to displace the ECP to a value that is more negative than the critical value for the component of interest under the prevailing conditions. In hydrogen water chemistry (HWC), which is a mitigation technique that is now being applied to operating reactors, molecular hydrogen is added to the feedwater with the objective of reducing the concentrations of oxidizing species (e.g. O_2, H_2O_2) and of displacing the ECP in the negative direction. One of the primary objectives in developing the chemistry/damage simulation codes was to provide a deterministically based technology for assessing the efficacies of various mitigation technologies without incurring the expense of extensive in-plant testing.

The original code (DAMAGE-PREDICTOR),[4-7)] from which ALERT was developed, incorporates deterministic modules for estimating the specie concentrations,[8)] the ECP,[13)] and crack growth rate (CGR)[9-12)] for stainless steel components at closely spaced points around the coolant circuit, as a function of coolant pathway geometry, reactor operating parameters (power level, flow velocity, dose rates, etc.), coolant conductivity, and the concentration of hydrogen added to the feedwater. The radiolytic species concentrations are calculated in the steady state using the radiolysis module, RADIOCHEM, which is based on a model that was originally developed to describe the corrosion of high-level nuclear waste containers.[8)] Calculation of the ECP was affected by the mixed potential model (MPM),[13),25)] which makes use of the fact that, for a system undergoing general corrosion (which is the process that establishes the ECP), the sum of the current densities due to all charge transfer reactions at the steel surface must be zero. By expressing the redox reaction currents in terms of the generalized Butler-Volmer equation, which incorporates thermodynamic equilibrium, kinetic, and hydrodynamic effects, and by expressing the corrosion current in terms of either the point defect model or as an experimentally derived function (both have been used), it is possible to solve the charge conservation constraint for the corrosion potential (ECP). The MPM has been extensively tested against experimental and field data and has been found to provide accurate estimates of the ECP.[1),25)]

The deterministic crack growth model (the CEFM)[9-11)] estimates the rate of growth of a crack at any point in the coolant circuit. The CEFM is deterministic, in that it satisfies the relevant natural law; the conservation of charge. Furthermore, a basic premise of the CEFM, that current flows from the crack and is consumed on the

external surface, has been demonstrated experimentally.[26),27)] To our knowledge, the CEFM and variants thereof (e.g. the CECFM) are the *only currently available models that satisfy the conservation of charge constraint explicitly*. The high degree of determinism is demonstrated by the fact that the models require calibration against only a single CGR/ECP/conductivity/temperature/stress intensity datum for a given degree of sensitization (DOS) of the steel.[11)]

The MPM and CEFM contain the necessary facilities for modeling noble metal enhanced hydrogen water chemistry (NMEHWC), as affected by the use of catalytic coatings (i.e. noble metals), and for modeling other advanced remedial measures such as dielectric coatings and ultra-low conductivity operation. A considerable achievement of the MPM and CEFM was the prediction that dielectric coatings represented a viable, and indeed an advantageous, alternative to noble metal coatings; a prediction that has been confirmed experimentally.[28)] The effectiveness of both strategies arises from modification of the exchange current densities for the redox reactions (oxidation of hydrogen and the reduction of oxygen and hydrogen peroxide) that occur on the steel surface.[6),29)] In the case of the noble metal coatings, the exchange current densities are increased, with the greatest increase occurring for the hydrogen electrode reaction. This renders hydrogen to be a much more effective reducing agent than it is in the absence of the noble metal, thereby making it much more effective in displacing the ECP in the negative direction. In the case of dielectric coatings, the lower exchange current densities render the metal less susceptible to the ECP-raising oxidizing species, with the result that the ECP is also displaced in the negative direction, even in the absence of hydrogen added to the feedwater.

DAMAGE-PREDICTOR has been used to model eleven operating BWRs, including Duane-Arnold, Dresden-2, Grand-Gulf, River-Bend, Susquehanna, Hamaoka-2, Leibstadt, Perry, and Fermi-2. Additionally, the code has been installed in computers at Fermi-2 and has been provided to researchers at the Argonne National Laboratory for use in their NRC-sponsored program on environmentally influenced cracking of reactor alloys in simulated BWR coolant environments. A "second-generation" code, REMAIN,[30)] has been developed for a German vendor to model BWRs with internal coolant pumps and a third generation code, ALERT, is now used to model BWRs with external pumps. All three generations of code have been validated by direct comparison with plant data (e.g. at the Leibstadt BWR in Switzerland), and are found to simulate accurately hydrogen water chemistry. The codes have also been used to explore various enhanced versions of HWC and to model completely new strategies, such as those that employ noble metal coatings and dielectric coatings. Two of the component models of these codes, in fact, *predicted* quantitatively the effectiveness of dielectric coatings for inhibiting crack growth in stainless steels in high temperature water, and these predictions have been validated by direct experiment.[27),28)]

The speed afforded by the enhanced ALERT code, which employs optimized mathematical algorithms and C++ programming language, permits near "real time" prediction of the accumulated damage (the crack length vs. time for a preconceived operating history). The accumulated damage is the *expected* crack length, L, which is calculated on a component-by-component basis as a function of the observation time, T, for an envisioned future operating protocol

$$L = \int_o^T \frac{\partial L}{\partial t} dt \tag{10}$$

Crack growth rates are calculated from the coupled environment fracture model as

$$\frac{\partial L}{\partial t} = f\left[power(t), chemistry(t), L(t)\right] \tag{11}$$

in which the dependencies on the first two independent variables arise from the impact of radiolysis, temperature, flow rate, and impurity concentration on the water chemistry experienced by the crack. However, it is extremely important that any model that is used in calculations of this type incorporates the impact of changing crack geometry, L(t), on the crack growth rate, as discussed below. The CEFM and variants thereof satisfy this condition.

The ALERT code calculates crack length, L, over the anticipated service life (T) of a component, as the accumulation of incremental crack advances over N periods of time $\Delta t_1, \cdots, \Delta t_i, \cdots, \Delta t_N$

$$L_i = L_{i-1} + \left(\frac{\partial L}{\partial t}\right)_i \Delta t_i \tag{12}$$

$$T = \sum_{i=1}^{N} \Delta t_i \tag{13}$$

The crack growth rate is assumed to be time-independent for each interval, Δt_i, which is a reasonable assumption provided that the increments are sufficiently small. The initial crack length, L_0, corresponds to the depth

of a pre-existing crack (as may have been detected during an inspection or assumed for a safety analysis scenario). The running time for simulating a typical ten-year operating period is less than 10 minutes on a desktop computer or on a notebook PC, and is less than a minute for simulating a single state point {water radiolysis + corrosion potential + crack growth rate}.

The importance of recognizing the impact of crack length on crack growth rate is illustrated by the following analysis. Thus, for an occluded crack under constant load, the crack growth rate is predicted to decrease with crack length (and hence time) as noted above. This is due to the fact that, as the crack length increases, a greater IR potential drop occurs down the crack and smaller potential drops occur across the crack tip and across the interfaces external to the crack, where the principal charge transfer reactions take place. Lower potential drops at these locations imply lower rates of reaction and hence lower crack propagation rate than what would be observed in the absence of the increase in the IR potential drop due to the increase in crack length. If this factor is ignored and a "linear" (or constant crack growth rate) approach is used to estimate L(t) as

$$L(t) = L_0 + \left(\frac{\partial L}{\partial t}\right)_{t=0} t \qquad (14)$$

the predicted crack length is significantly overestimated. As an example, we compare the predictions of ALERT and a "linear" approach for the propagation of the same 0.5 cm deep crack in a BWR core shroud over 24 calendar months of operation (two fuel cycles including outages), as shown in Fig. 2. The accumulated crack depth, as estimated by the ALERT algorithm, is about 1.5 cm (which is in excellent accord with actual in service inspection data reported recently in Ref 31). On the other hand, the linear extrapolation of the crack propagation yields 2.9 cm or twice that estimated by ALERT. This difference is significant, and it is not surprising that reactor operators lose confidence in models that predict "failure" well before it actually occurs.

As an example of the prediction of accumulated damage in an operating BWR, we show in Fig. 3 predicted crack depth versus time for a crack in the core shroud inner surface above the core midplane. The crack was assumed to have an initial depth of 0.5 cm and to be characterized by an initial stress intensity factor of 27.5 MPa. m (a constant stress is also assumed, so that K_I increases as the crack grows). Once the length of a crack at a given location exceeds the physical dimension of the component

Fig. 2. Illustration of the nonlinearity of the accumulated damage and inadequacy of the linear approach for extrapolating crack propagation for future operating periods(regular and identical outages and fuel cycles).

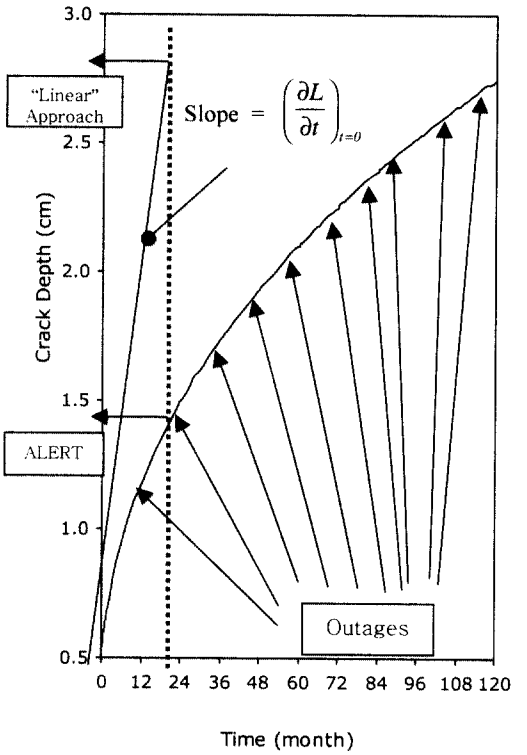

Fig. 2. Illustration of the nonlinearity of the accumulated damage and inadequacy of the linear approach for extrapolating crack propagation for future operating periods(regular and identical outages and fuel cycles).

or exceeds the critical value corresponding to $K_I > K_{IC}$, failure of the component is deemed to have occurred. We refer to these two cases as being "damage-controlled" and "stress-controlled" failures, respectively. It is important to note that, even when the stress intensity increases with time, the crack growth rate is predicted to decrease over the same period. This is a consequence of the negative impact of increasing crack length on the current and potential distributions within the internal and external crack environments, and hence on the crack growth rate, as predicted by the CEFM,[11] being more important than the small positive impact of KI on the crack growth rate in the Stage II region.

The actual impact that increasing crack length has on the crack growth rate is predicted to be a function of conductivity, ECP, flow rate (even for a high aspect ratio crack), and stress intensity.[11),27)] Accordingly, the predicted accumulated damage becomes a sensitive, nonlinear function of the operating history of the reactor, in a manner that is unlikely to be captured by empirical models.

The impact that hydrogen water chemistry (HWC) is predicted to have on the accumulated damage is illustrated in Fig. 3. Thus, an immediate addition of 1 ppm ($0.5x10^{-3}$

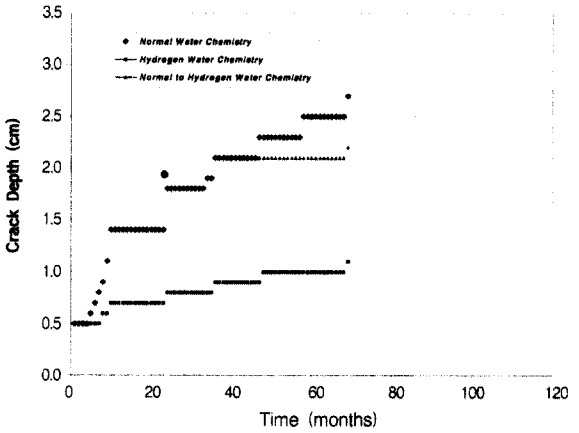

Fig. 3. Predicted histories of a growing crack in the core shroud of an operating Boiling Water Reactor as a function of preconceived future operating histories. Note that the discontinuities in the crack length arise from changes in crack growth rate during outages (irregular outages).

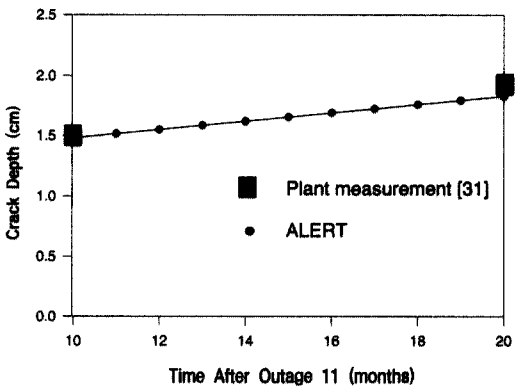

Fig. 4. Depth of the crack in the H-3 weld monitored by Tang, et. al.[31] in an operating BWR as a function of time after Outage 11. The calculated and measured depths at ten months were made to coincide by adjusting the initiation time, so that only the comparison at 20 months has value.

mol/kg) of H_2 to the feedwater is predicted to decrease the increment in accumulated damage in the core shroud after ten years of operation by a factor of about 4, from 2.2 cm to about 0.5 cm. This is a substantial reduction in the extent of damage that could not have been estimated from the crack growth rates at a single state point alone (because of the different, non-linear dependencies of crack growth rate on time), or by using a model that fails to recognize a dependence of crack growth rate on crack length. The same level of hydrogen addition implemented five years later is predicted to yield much smaller benefits for the considered component and location. Thus, an optimal implementation time may be derived for a given reactor by selecting a HWC initiation time that provides for the most cost effective operation in the future in light of other (technical and economic) factors.

As an indication of the accuracy that can be achieved in predicting the accumulation of SCC damage in an operating reactor, we show in Fig. 4 a comparison of the calculated increase in length of a crack in the H-3 weld in the inner surface of a BWR core shroud with the observed value, as determined by inspection.[31] The level of agreement is considered to be excellent, considering that estimates had to be made of many parameters (e.g. stress and water conductivity).

Our work to date has emphasized BWRs, because that is where the greatest need has been in assisting plant operators to specify the most cost-effective operating protocols. However, we have also employed two of the modules (RADIOCHEM and the MPM) of the three generations of codes that have been developed in our program for modeling the primary coolant of commercial pressurized water reactors (PWRs), with the goal of specifying the coolant conditions ([H_2], [B], [Li], T) under which cracking of steam generator tubes and other susceptible components might be avoided.[32]

4. Summary and conclusions

The rate of development of damage is almost always a strong function of the history of operation. Accordingly, industrial systems and plants that are nominally identical quickly become unique, due to unique operating histories and conditions. This uniqueness, coupled with the fact that failures are generally rare events, means that, in most cases, insufficient statistical failure data are available to devise effective empirical models for predicting the onset and evolution of localized corrosion damage. In most cases, one essentially needs to know the answer about the development of damage in advance before predictions can be made. Clearly, in these cases, empirical methods are of marginal value. The alternative philosophy is determinism, in which prediction is made on the basis of mechanism-based physical and chemical models whose outputs are constrained by the natural laws.

In this paper, the foundations of the deterministic prediction of damage due to localized corrosion have been outlined, including the theoretical bases for predicting a complete cycle of damage development: the nucleation, growth, and death of individual events (pits/cracks) and the evolution of damage in an ensemble of events occurring in a progressive manner. Damage is expressed in terms of integral damage functions, which are histograms of event frequency vs. incremental depth. The application of damage function analysis (DFA) has been

illustrated with reference to the prediction of pitting damage on aluminum in chloride-containing solution and with reference to the accumulation of damage due to stress corrosion cracking in water-cooled nuclear power reactors.

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