

# Unification of the Theories for Stress Corrosion Cracking and Corrosion Fatigue

*G.R. Engelhardt*

*OLI Systems, Inc.,*

*108 American Road, Morris Plains, NJ 07950*

*D. D. Macdonald<sup>1</sup>*

*Center for Electrochemical Science and Technology,*

*Dept. Materials Science & Engineering, Pennsylvania State University,*

*University Park, PA 16802*

## **Abstract**

The application of standard mathematical techniques for the solution of mass transport equations, in the case of advection that is caused by the pulsating movement of crack walls in the case of corrosion fatigue, can be very time consuming. This problem arises, due to the requirement that the time step that must be employed, when solving the non-stationary equations, must be significantly smaller than the period of oscillation. For overcoming these time-consuming limitations, a simple algorithm, which is based on eliminating the convective term from the equations of mass transfer in the pulsating slab by a suitable change of variables, was developed. It is shown that, in many cases, it is possible to use codes that were developed for describing stress corrosion cracking, i.e. for the case of mass transfer without advection, to predict corrosion fatigue crack propagation rate, by simply substituting an effective crack length.

Keywords: corrosion fatigue, stress corrosion cracking, crack growth rate, advection

## **1. Introduction**

Fatigue/crack propagation under periodical mechanical loading in an aqueous environment is a direct result of electrochemical and chemical reactions occurring within the cavity and on the external surfaces. The rates of these reactions and, accordingly, the influence of the reactions on fatigue crack growth rate, depend on the local specie concentrations, temperature, and electrode potential that, in turn, depend on mass and charge transfer between the cavity the bulk. In the literature, there can be found several studies devoted to modeling of the electrochemistry of corroding cavities (see, for example, [1-6]) and of crack propagation rate (see, for example, [7]) under corrosion fatigue conditions (periodic loading). The mathematical description of mass transfer in corrosion fatigue cracks is much more complicated than in the corresponding problem under

---

<sup>1</sup> Corresponding author; ddm2@psu.edu

constant load in the case of stress corrosion cracking, due to the presence of advection (fluid flow induced by the cyclic displacement of crack walls). The advection term that arises in the mass balance equations does not allow us to obtain analytical solutions even for the simplest cases. Moreover, because the hydrodynamic component changes direction during a cycle, it is difficult even to predict whether the advection inhibits or enhances propagation of the crack (below we show that both possibilities are predicted).

Advection also greatly complicates the numerical solution of the mass transfer equations by complicating the finite difference schemes that are commonly employed [8] and forces the modeler to use very small time steps, especially at high frequency,  $f$ , of wall oscillation. Thus, in the simplest case of a parallel-walled slot with passive sides and an active tip, the time taken for the system to approach steady state distributions in species concentrations, and hence potential within the cavity, is of the order of  $t_{st} \approx L^2/D$ , where  $L$  is the crack depth and  $D$  is the diffusion coefficient of the corroding metal ions (it is assumed that the initial concentrations coincide with their bulk values) [9]. If, for example,  $L = 1$  cm and  $D = 10^{-5}$  cm<sup>2</sup>/s we have  $t_{st} \approx 10^5$  s. Accordingly, the time step  $\Delta t$  in any numerical calculations for diffusional transport must be much less than  $t_{st}$ . Usually the value of  $\Delta t \approx 10^{-2} t_{st}$  is sufficiently small for obtaining satisfactory accuracy by applying the usual fully implicit finite difference scheme and, in our case, we have taken  $\Delta t \approx 10^3$  s. The situation is dramatically changed in the presence of advection. It is evident that, in order to fully describe advection, the time step  $\Delta t$  must be much less than the period of oscillation  $T = 1/f$  of the moving walls (let say by factor 10). This means that if, for example,  $f = 100$  Hz, a time step of the order of  $10^{-3}$  s must be used in this case, *i.e.* the number of time steps (the volume of calculations) increases by a factor of  $10^6$  in comparison with the absence of advection. Accordingly, practically in all published works, the numerical calculations were performed for relatively low loading frequencies and hence for low frequency pulsation of the crack flanks,  $f$ , actually for the range  $f \leq 10$  Hz. However, as is well known, in the case, for example, of low pressure steam turbines, the blades flex at their natural frequencies. These frequencies may range from 75 Hz (for the lowest mode of a low-pressure blade), to 400 Hz or more. In addition, high-cycle corrosion fatigue experiments at relatively high frequencies (up to 100 Hz) are often conducted to conserve time and the results are often extrapolated from high frequencies to lower frequencies. It must also be noted that the solution of the transport equations, even for the case of low frequencies,  $f \approx 0.1-1$  Hz, becomes so time consuming that one is forced to obtain the results of the calculations for only a limited range of parameters [2].

This paper describes a simple algorithm that is based on the eliminating the convective term from the equations of mass transfer in the pulsating slab by a suitable change of variables. In this case, for simplicity, we consider active metal dissolution only at the tip of the crack, with the passive current on the crack flanks being assumed to be insignificant (the same approximation was used, for example, in Refs. 2 and 8). More precisely, we consider the case when the concentration of the dissolved metal ions at the crack tip is fixed (for, example,

when it equals the saturation concentration of some precipitated phase) and the case when active dissolution at the crack tip is described by Tafel kinetics.

## 2. Transformation of variables

In this paper, we will consider the simplest case when metal is dissolved at the tip of the long parallel slot with pulsating walls moving in accordance with the equation:

$$w(t) = w_m g(t) \quad (1)$$

where  $t$  is the time,  $w$  is the width of the parallel-walled crack,  $w_m$  is the average width of the crevice over the period of oscillation and function  $g$  must satisfy three important conditions:

$$g(t+T) = g(t), \quad g_{\min} \leq g(t) \leq g_{\max}, \quad \frac{1}{T} \int_0^T g(t) dt = 1 \quad (2)$$

where  $0 < g_{\min} \leq 1$  and  $g_{\max} \geq 1$  are minimum and maximum values of the function  $g(t)$ , respectively. These conditions mean that the function  $g(t)$  is periodical with the period,  $T$ , and that  $w_m$  is really the mean value of  $w(t)$  over the period of oscillation. Particularly, in the case of the present analysis, we consider harmonic loading and hence

$$g(t) = 1 + \varepsilon \sin(\omega t) \quad (3)$$

where  $\omega = 2\pi f$  is the cyclic loading angular frequency and  $\varepsilon < 1$  is a known constant.

The movement of the walls results in a corresponding movement of liquid within the crevice with the velocity,  $V$ , (averaged across the width of the crack), which can be found from the equation of continuity (conservation of mass for incompressible liquid flow) in the one dimensional approximation as

$$\frac{\partial w}{\partial t} + \frac{\partial(Vw)}{\partial x} = 0, \quad (4)$$

where  $x$  is the distance from the tip of the crevice. For a parallel slot the velocity of the fluid within the cavity can be written as

$$V(x, t) = -\frac{1}{w(t)} \int_0^x \frac{\partial w}{\partial t} dx = -\frac{\dot{g}(t)}{g(t)} x, \quad (5)$$

Furthermore, in a one-dimension approximation, the equation of mass transport for a species in the solution has the form

$$\frac{\partial(wC_k)}{\partial t} = -\frac{\partial(wN_k)}{\partial x} + wR_{V_k} + 2N_{s_k} \quad (6)$$

where  $C_k$  is the concentration of species  $k$ ,  $N_k$  is the flux density,  $R_{V_k}$  is the rate of creation of ionic species,  $k$ , per unit volume, and  $N_{s_k}$  is the flux of species  $k$

through the metal-solution interface on the side walls. According to dilute solution theory, the flux of species,  $k$ , is given by the Nernst-Planck equation:

$$N_k = -D_k \left[ \frac{\partial C_k}{\partial x} + \frac{z_k F}{RT} C_k \frac{\partial \varphi}{\partial x} \right] + C_k V \quad (7)$$

where  $D_k$  is the diffusion coefficient,  $z_k$  is the charge number on the ion,  $T$  is the temperature,  $R$  is the gas constant, and  $\varphi$  is the electrostatic potential. The solution is assumed to be electrically neutral, so that

$$\sum_k z_k C_k = 0 \quad (8)$$

In Equations (6)-(8) all unknown concentrations and potential are considered to be averaged over the crack gap at any time.

In the simplest case, neglecting chemical reactions, and electrochemical reactions on the crack sides, and taking into account Equation (5) for the hydrodynamic velocity, we can present the equation of mass transfer for the ions in the parallel pulsating crevice as follows:

$$\frac{\partial C_k}{\partial t} - \frac{\dot{g}(t)}{g(t)} x \frac{\partial C_k}{\partial x} = D_k \frac{\partial^2 C_k}{\partial x^2} + \frac{F z_k}{RT} \frac{\partial}{\partial x} C_k \frac{\partial \varphi}{\partial x} \quad (9)$$

The boundary conditions for the concentrations at the crack mouth are evident:

$$C_k = C_{k,0} \quad \text{at} \quad x = L \quad (10)$$

where  $C_{k,0}$  is the bulk concentration of Species  $k$ , and  $L$  is the length of the crack. The boundary conditions at crack tip (at  $x = 0$ ) will be discuss below, and the initial conditions can be arbitrary, because only the steady-state solution (at  $t \rightarrow \infty$ ) is of interested to us in this analysis.

The expression for convective mass transfer, Equations (13), can be reduced to the equations for diffusion-migration mass transfer

$$\frac{\partial C_k}{\partial \tau} = D \frac{\partial^2 C_k}{\partial y^2} + \frac{F z_k}{RT} \frac{\partial}{\partial y} C_k \frac{\partial \varphi}{\partial y} \quad (11)$$

if we introduce the new variables:

$$\tau = \int_0^t g^2(t') dt', \quad y = xg(t) \quad (12)$$

For the case of harmonic oscillation, Equations (12) yield:

$$\tau = \left( 1 + \frac{\varepsilon^2}{2} \right) t + \frac{2\varepsilon}{\omega} [1 - \cos(\omega t)] - \frac{\varepsilon^2}{4\omega} \sin(2\omega t), \quad y = x[1 + \varepsilon \sin(\omega t)] \quad (13)$$

Boundary Condition (10), in terms of the new variables, has the form

$$C = C_{k,0} \quad \text{at} \quad y = Lg(t) \quad (14)$$

In Boundary Condition (14), the old time,  $t$ , must be expressed via the new time,  $\tau$ , by using Equations (13). Thus, in the case of harmonic oscillation, it is evident that, after a very short initial (transient) period, we have

$$t = \tau / (1 + \varepsilon^2 / 2) \quad (15)$$

Equations (11), together with the boundary conditions describes the mass transfer between the plane at  $y = 0$  (which corresponds the boundary condition at  $x = 0$ ) and the plane that periodically moves between points  $Lg_{min}$  and  $Lg_{max}$  (where concentrations  $C_{k,0}$  is assumed to exist). Thus, in the case of the harmonic movement of the crack sides, this plane moves according to  $y = L[1 + \varepsilon \sin(\omega' \tau)]$  (where concentrations  $C_{k,0}$  is assumed to exist). Here, in accordance with Equation (15), we denote  $\omega' = \omega / (1 + \varepsilon^2 / 2)$ . Intuitively, it is clear (and it is confirmed by numerical calculations) that, if the frequency of the movement of this plane is sufficiently high, the region  $[Lg_{min}, Lg_{max}]$  ( $[L(1-\varepsilon), L(1+\varepsilon)]$  in the harmonic case) can be considered as being kept at concentrations  $C_{k,0}$ . This means that, for the region  $[Lg_{min}, Lg_{max}]$ , Boundary Condition (14) can be replaced by the following:  $C = C_{k,0}$  at  $y = Lg_{min}$ .

### 3. Examples of application of the transformation of variables

Firstly, let us consider the simplest case when dissolution of the metal occurs to produce a saturated solution of the metal cation of concentration,  $C$ , in the presence of an indifferent electrolyte and that the rate of the reaction is under diffusion control. In this case, the boundary condition at the crack tip (at  $x = y = 0$ ) is given,

$$C = C_s \quad \text{at} \quad y = 0 \quad (16)$$

In accordance with the previous discussion, the steady-state solution at high frequencies has the form:

$$C = C_s + \frac{C_0 - C_s}{Lg_{min}} y \quad \text{at} \quad y \leq Lg_{min} \quad \text{and} \quad C = C_0 \quad \text{at} \quad Lg_{min} \leq y \leq Lg_{max} \quad (17)$$

or, in terms of the physical variables,  $x$ ,  $t$ , we have for the steady-state conditions

$$C = C_s + \frac{C_0 - C_s}{Lg_{min}} xg(t) \quad \text{at} \quad x \leq \frac{Lg_{min}}{g(t)} \quad (18)$$

and  $C = C_0$  at  $Lg_{min} / g(t) \leq x \leq L$

Numerical calculations confirm this assumption [i.e., Equation (2)], even for  $f = 1$  Hz (see Figure 1). The numerical solution of the diffusion equation was performed by using the standard finite difference method for the region  $[0 \leq y \leq L(1+\varepsilon)]$  by assuming that  $C = C_0$  at  $y = L(1+\varepsilon)$  and that the diffusion coefficient

$D$  is a very large number in the region  $y \geq L[1+\varepsilon\sin(\omega t)]$ . This condition is equivalent to Boundary Condition (14).

Accordingly, the current density at the crack tip is given by

$$i = -z_1FD \left( \frac{\partial C}{\partial x} \right)_{x=0} = -z_1FD \left( \frac{\partial C}{\partial y} \right)_{y=0} g(t) = z_1FD \frac{C_s - C_0}{Lg_{\min}} g(t) \quad (19)$$

Averaging of the current density over the period of oscillation,  $T = 1/f$ , yields

$$i_{av} = \frac{1}{T} \int_0^T i dt = z_1FD \frac{C_s - C_0}{Lg_{\min}} \quad (20)$$

This relationship implies that, under the assumed conditions, the averaged current density in the crack with advection corresponds to the current density in the crack without advection (i.e., under constant loading conditions), but with a reduced effective crack length  $L_{eff} = Lg_{\min}$ . In other words, the rate of corrosion increases by the factor

$$i_{av}/i_d = 1/g_{\min} \quad (21)$$

[(i.e., by the factor  $1/(1-\varepsilon)$  in the harmonic case), where,  $i_d$ , is the diffusion current density, calculated in the absence of convection (i.e., for a motionless crevice). It is evident that Relation (21) holds also in the case of the metal corrosion in its own salt.

It is also important to clarify the meaning of ‘‘a sufficiently high frequency’’. In order to do so, it is convenient to present the boundary problem in dimensionless form by introducing the dimensionless depth  $y^* = y/L$  and dimensionless time  $\tau^* = \tau D/L^2$ . It can be easily shown that the dimensionless value  $i_{av}/i_d$  depends only on two dimensionless parameters:  $\varepsilon$  and dimensionless frequency

$$f^* = \frac{fL^2}{(1 + \varepsilon^2/4)D} \quad (22)$$

The results of numerical calculations are shown in Figure 2. We see that, for  $f^* \geq 10^5$ , the results of the calculations practically coincide with the asymptotic solutions (for  $f^* \rightarrow \infty$ ). Thus, for  $D = 10^{-5}$  cm/s and  $L = 1$  cm, this condition corresponds to a dimensioned frequency,  $f$  of the order of 1 Hz. However, some reasonable approximation (with the accuracy of order 10-20 %) can be obtained even for  $f^* \geq 10^3$  that corresponds to  $f$  being of the order of 0.01 Hz.

Above, the case of diffusion limitation, when the concentration of the active species at the crevice tip is fixed (for example due to the attainment of saturation), has been considered. However, in the majority of cases, the current density at the crack tip depends on the potential at the tip (and, in the general case, on the concentrations of some species near crack tip that are involved in the kinetics of the dissolution reaction). Here, we consider the simplest case when the corrosion current density at the crack tip,  $i$ , is described by Tafel’s law and, accordingly, can be presented in the form:

$$i = i_m \exp\left(-\frac{\alpha F \Delta \varphi}{RT}\right) \quad (23)$$

where  $i_m$  is the corrosion current density that corresponds to the potential at the mouth of the crack,  $\Delta \varphi$  is the potential drop in the crack, and  $\alpha$  is the anodic transfer coefficient. It is important to note that, in the general case, in accordance with the slip dissolution model,  $i_m$  can be presented in the form of  $i_m = i_m^0 \Gamma$ , where  $i_m^0$  is the corrosion current density at the bare surface and  $\Gamma$  is the averaged ratio of the bare surface to the total geometrical area of the dissolving crevice tip [10]. For pitting corrosion,  $\Gamma = 1$ , and for stress corrosion cracking or corrosion fatigue  $\Gamma$  can be estimated from [10]

$$\Gamma = \frac{t_0^n \dot{\varepsilon}_{ct}^n}{(1-n)\varepsilon_f^n} \quad (24)$$

where  $t_0$  is the time of exposure of the bare surface prior to repassivation,  $n$  is the current decay constant, and  $\varepsilon_f$  is the fracture strain of the passive film at the crack apex. The value of the crack tip strain rate,  $\dot{\varepsilon}_{ct}$ , can be found, for example, from Congleton's correlation [11]. Some other expressions for  $\dot{\varepsilon}_{ct}$  can be found in Review 12.

Previously, we proposed a simplified method for calculating corrosion cavity propagation rates [13]. This method is based on the postulate that, if the rate of an electrode reaction depends (in an explicit form) only on the potential, the pit growth rate depends only on the concentration of those species that determine the potential distribution near the metal surface within the cavity. In particular, it has been shown that under commonly experienced conditions, in the case of the dissolution of Fe in NaCl solution, only  $\text{Fe}^{2+}$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  are of importance, if we wish to calculate the crack propagation rate [and the presence of other species, like  $\text{H}^+$ ,  $\text{OH}^-$  and  $\text{Fe}(\text{OH})^+$  can be ignored]. This assumption, of course, is valid only if the crevice does not become too acidic, in which case  $\text{H}^+$  becomes important as well. Moreover, it was shown that the potential distribution (and, accordingly, crack propagation rate) differs little from that obtained for the case when only  $\text{Fe}^{2+}$  and  $\text{Cl}^-$  are present in the solution (i.e. in a binary system). Of course, it is assumed that the bulk concentration of  $\text{FeCl}_2$  must be equal to half of the bulk concentration of NaCl, because the bulk concentration of  $\text{Cl}^-$  must be the same.

Under these conditions, the concentration of  $\text{Fe}^{2+}$ , ( $C_1$ ) and  $\text{Cl}^-$  ( $C_2$ ), are described by Equations (11) with boundary conditions:

$$-z_1 F D_1 \frac{\partial C_1}{\partial y} = \frac{i_m}{z_1 F} \exp(-\alpha F \varphi / RT) / g(t), \quad \frac{\partial C_2}{\partial y} = 0 \quad \text{at } x = 0 \quad (25)$$

Figure 3 shows that, at sufficiently high frequency, and after a sufficiently long period of time (corresponding to the establishment of the steady-state), the concentration distribution does not depend on time when expressed in terms of the variables  $y$  and  $\tau$ . The concentration depends linearly on the distance coordinates

in the region  $y \leq Lg_{\min}$  and equals the corresponding bulk value for  $Lg_{\min} \leq y \leq Lg_{\max}$ . This finding means that, at sufficiently high frequency, the steady state concentration cannot follow the oscillation of the plane  $y = Lg(t)$  and the periodical component of the mass flux at the metal surface. Many examples confirming this fact can be found, for example in Ref. 9 for the equivalent heat transfer problem.

The potential drop in the cavity at high frequencies, averaged over the period of oscillation,  $\Delta\varphi$ , can be estimated as a sum of two terms:  $\Delta\varphi = \Delta\varphi_1 + \Delta\varphi_2$ , where  $\Delta\varphi_1$  is the averaged potential drop inside the region  $y \leq Lg_{\min}$  and  $\Delta\varphi_2$  is the averaged potential drop in the region  $Lg_{\min} \leq y \leq Lg_{\max}$ . It can be shown that [13]

$$\Delta\varphi_1 = \frac{RT}{F} \text{Ln} \left\{ 1 + \frac{i_m \exp(-\alpha F \Delta\varphi / RT) Lg_{\min}}{(1 - z_1 / z_2) z_1 D_1 F C_0} \right\} \quad (26)$$

where  $C_0$  is the bulk concentration of the salt ( $\text{FeCl}_2$ ). Because the concentration inside  $Lg_{\min} \leq y \leq Lg_{\max}$  can be considered as being constant, we can calculate  $\Delta\varphi_2$  by using Ohm's law for the region between the planes at  $y = Lg_{\min}$  and  $y = Lg(t)$ . In accordance with the third Condition (2), the average distance between  $y = Lg_{\min}$  and  $y = Lg(t)$  equals  $L(1 - g_{\min})$  ( $L\varepsilon$  in the harmonic case), i.e.

$$\Delta\varphi_2 = i_m \exp(-\alpha F \Delta\varphi / RT) L(1 - g_{\min}) / \kappa_0 \quad (27)$$

where  $\kappa_0$  is the bulk conductivity of the electrolyte

Accordingly, the averaged potential drop inside the cavity,  $\Delta\varphi$ , can be found via numerical solution of the equation:

$$\Delta\varphi = \frac{RT}{F} \text{Ln} \left\{ 1 + \frac{i_m \exp(-\alpha F \Delta\varphi / RT) Lg_{\min}}{z_1 (1 - z_1 / z_2) D_1 F C_0} \right\} + i_m \exp(-\alpha F \Delta\varphi / RT) L(1 - g_{\min}) / \kappa_0 \quad (28)$$

which can be easily affected by using any standard method.

By using Equation (23), we can rewrite Equation (31) relative to the value of  $i_{av}/i_m$ , in the form

$$i_{av} / i_m = \left\{ 1 + A(i_{av} / i_m) g_{\min} \right\}^{-\alpha} \exp[-B(1 - g_{\min})(i_{av} / i_m)] \quad (29)$$

where

$$A = \frac{Li_m}{z_1 (1 - z_1 / z_2) D_1 F C_0}, \quad B = A\alpha(1 - z_1 / z_2) t_1 / z_1 \quad (30)$$

which can be easily solved numerically.

In the absence of advection,  $g_{\min} = 1$ , and Equation (29) reduces to

$$i_d / i_m = \left\{ 1 + A(i_d / i_m) \right\}^{-\alpha} \quad (31)$$



i.e. to the corresponding equation for calculating corrosion crack current density,  $i_d$ , in the absence of convection [13]. Figure 4 illustrates the influence of advection on the averaged current density in the case of corrosion fatigue. Calculations were based on the numerical solution of Equation (29) and (31) and they differ by no more than 2 % from the results of the direct numerical solution of the equation of convective diffusion, which requires a great deal of calculation time.

#### 4. Discussion

It has been tacitly assumed, so far in our analysis, that, for the case of a sufficiently deep crack, it is possible to neglect the potential drop in the external environment and to calculate the potential distribution,  $\varphi$ , by solving the balance equations inside the crack only; i.e. we assumed that metal potential at the crack mouth coincides with the corrosion potential of the metal on the external surface. This assumption can lead to significant conceptual and numerical errors (especially at low concentration of bulk electrolyte), because the system has not been constrained by the conservation of charge and hence lacks the condition that renders the model deterministic. However, it has been experimentally demonstrated that, in the case of SCC at least, and almost certainly in the case of corrosion fatigue also, a coupling current flows from the slot to the external surfaces, where it is annihilated by the reduction of oxygen, indicating that a potential gradient must exist in the external environment. In accordance with the general theory for stress corrosion cracking, as embodied by the Coupled Environment Models (see, for example [13]-[15]), which take into account the influence of the external environment, and for which the predicted crack growth rate is constrained by the conservation of charge, the potential drop between the crack tip and a point on the external environment that is remote from the crack mouth can be taken into account by adding to the potential drop inside the cavity,  $\Delta\varphi_{in}$ , the potential drop in the external environment,  $\Delta\varphi_{ex}$ . Generally speaking,  $\Delta\varphi_{ex}$  can be expressed in the form

$$\Delta\varphi_{ex} = Q \frac{i_w}{\kappa_0} \quad (32)$$

The dimensionless parameter,  $Q$ , can be found analytically in some simplest of cases [13, 15], but, in the general case, it must be found by solving Laplace's equation for the external environment by some iterative process [14]. Recognition and inclusion of the potential drop in the external environment imparts determinism to the model, as previously emphasized [13] - [15].

Accordingly, in the general case, instead of Equation (28), we must solve the following equation

$$\begin{aligned} \Delta\varphi = & \frac{RT}{F} \text{Ln} \left\{ 1 + \frac{i_m \exp(-\alpha F \Delta\varphi / RT) L g_{\min}}{(1 - z_1 / z_2) D_1 F C_0} \right\} + i_m \exp(-\alpha F \Delta\varphi / RT) L (1 - g_{\min}) / \kappa_0 \\ & + Q \frac{i_m \exp(-\alpha F \Delta\varphi / RT) w_m}{\kappa_0} \end{aligned} \quad (33)$$

For the potential drop,  $\Delta\varphi$ . This means that solving the problem of mass transfer in the case of corrosion fatigue for a crevice in the form of a parallel-sided slot with passive sides at high oscillation frequency is equivalent to solving the mass transfer problem for a crevice without advection having an effective depth of

$$L_{eff} = Lg_{\min} \quad (34)$$

and having an effective parameter,  $Q_{eff}$ , of

$$Q_{eff} = Q + \frac{L(1 - g_{\min})}{w_m} \quad (35)$$

It is important to note that if we neglect the potential drop in the external environment, the corrosion current density (crack propagation rate) does not depend on the average width of the crack. However, if the potential drop outside the crevice is significant, such a dependence exists, as indicated by Equation (36), because the last term on the right side depends upon  $w_m$ .

We see that advection increases the corrosion current density, when we have diffusion limitation in the crack [see Equation (21)], but advection primarily reduces the corrosion current density in the case of mixed kinetics [see Figure 4]. The explanation is that advection decreases the concentration of the electrolyte near the crevice mouth (due to the mixing of electrolyte) and in doing so increases the resistance (and, hence, the potential drop) in the solution.

Our calculations show that, in contrast to the pulsating effects in the boundary conditions, in the case of normal diffusion, which disappear at high frequencies the advection effect increases with increasing applied frequency,  $f$ , and goes to some limit at  $f \rightarrow \infty$  (see Figure 3). It must also be noted that our current analysis does not take into account possible viscosity effects [2] that can, in turn, reduce the advection effect. Generally speaking, our calculations (for  $f \rightarrow \infty$ ) yield an estimate for the maximum possible influence of advection on the transport processes in the corrosion fatigue crevice.

It is important to mention that the method of predicting the CF crack growth rate described in this paper is also applicable to the case of a pulsating parallel slot with active walls, to the case of an arbitrary number of species in the solution, and to the case of arbitrary numbers of chemical and electrochemical reactions. Thus, after substitution of Equations (7) into Equation (6) and changing variables, we have the following equation for mass balance in a one dimensional approximation for a pulsating parallel slot

$$\frac{\partial C_k}{\partial \tau} = D \frac{\partial^2 C_k}{\partial y^2} + \frac{Fz_k}{RT} \frac{\partial}{\partial y} C_k \frac{\partial \varphi}{\partial y} + \frac{R_k}{g^2} + \frac{2N_s}{w_m g^3} \quad (36)$$

Comparing this equation with the equation of mass transfer in the one dimensional approximation for a parallel-sided slot without advection, we see that these equations coincide if we increase the rates of the chemical reactions by the factor  $1/g^2$  and rates of the electrochemical reactions by the factor  $1/g^3$ . For the case of high frequency, it is possible simply average values  $1/g^2$  and  $1/g^3$  over the

period of oscillation. It is possible to use the codes that have already been developed [13, 14] for estimating stress corrosion cracking crack growth rate after this formal substitution for describing corrosion fatigue, at least for the cases that have been considered in this paper (parallel pulsating slot). Of course, it must be recognized that, in accordance with the slip dissolution model, part of the geometrical surface area of the crack tip must be blocked by the passive film, and hence that the averaged ratio of the bare surface to the total geometrical area of the dissolving crevice tip as a function of strain rate has a different form for the case of corrosion fatigue than for stress corrosion cracking.

Finally we note that the change in variable method for solving the advection problem is also beneficial even for the case of arbitrary pulsating frequencies (and not just high frequencies). Thus, elimination of the convective terms from the equation of mass balance can significantly simplify the numerical solution of the mass balance equation when using finite difference methods (see, for example Ref. 8).

## 5. Conclusions

It has been shown that, in the general case, it is necessary to take into account transport processes (and potential drops) inside corrosion cracks when subjected to periodic (corrosion fatigue) or constant (stress corrosion cracking) loading. By neglecting such properties, errors of orders of magnitude may be induced in the calculated crack propagation rate. The application of standard mathematical techniques for the solution of mass transport equations, in the case of advection that is caused by the pulsating movement of crack walls under corrosion fatigue loading conditions, can be very time consuming. This problem arises, due to the requirements that the time step that must be employed when solving the non-stationary equations must be significantly smaller than the period of oscillation. For overcoming these time consuming limitations, a simple algorithm, which is based upon eliminating the convective term from the equations of mass transfer in a pulsating parallel-sided slot, by a suitable change of variables, was developed. It is shown that, in many cases, it is possible to use codes that were developed for describing stress corrosion cracking, i.e. for the case of mass transfer without advection, to describe corrosion fatigue, by simply substituting for an effective, frequency-dependent crack length and for the average fractional coverage of the crack tip by the passive film.

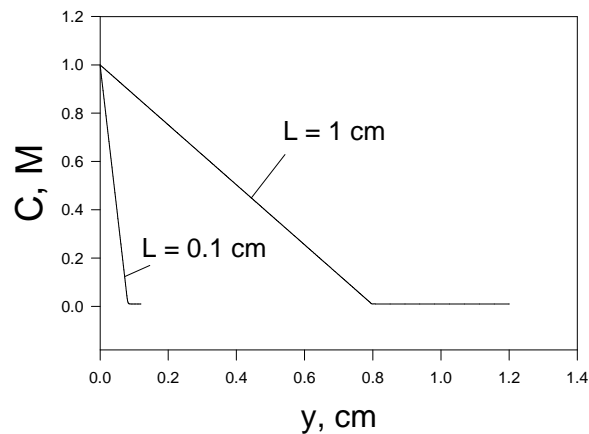
## 6. Acknowledgements

The authors gratefully acknowledge the support of this work by EPRI, Contract No. 2712-25, and DOE/Environmental Management Science Program, Contract No. DE-FG07-97ER62515.

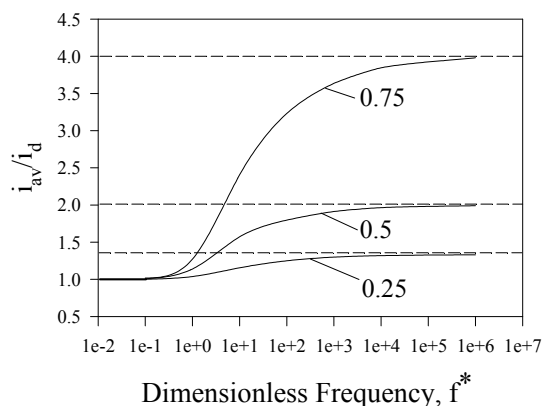
## 7. References

1. A. Turnbull, *Corros. Sci.*, **22**, 877 (1982).
2. A. Turnbull, *Mater. Sci. Technol.*, **1**, 700 (1985).

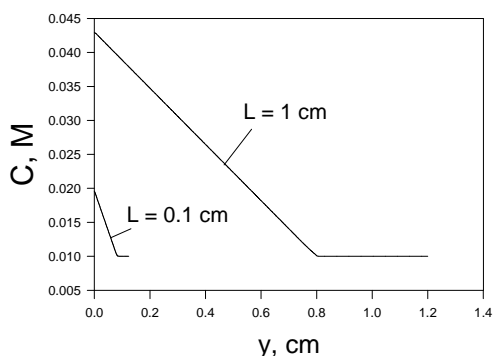
3. A. Turnbull and D. H. Ferris, *Corros. Sci*, **26**, 601 (1986).
4. A. Turnbull and D. H. Ferris, *Corros. Sci*, **27**, 1323 (1987).
5. H. En-Hou and Ke Wei, *Corros. Sci*, **35**, 599 (1993).
6. G. Engelhardt, and D. D. Macdonald, "Modeling of Corrosion Fatigue Chemistry in Sensitized Steel in Boiling water Reactor Environment." Corrosion'2000, Paper # 00227, pp. 1-12, Orlando, FL: NACE International, (March 2000)
7. G. Engelhardt, and D. D. Macdonald. "Modeling of Corrosion Fatigue Crack Propagation." Corrosion'2001, Houston, TX: NACE International, 2001.
8. D. H. Ferris. "Numerical solution of the advection-diffusion equation in a corrosion fatigue crack". Report DNA(A) 31, National Laboratory. Teddington, 1981.
9. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford, Clarendon Press, (1959).
10. D. D. Macdonald, *Corros. Sci.*, **38**, 1003 (1996).
11. J. Congleton, T. Shoji, and R. N. Parkins, *Corros. Sci.*, **26**, 163 (1985).
12. A. Turnbull, *Corros. Sci.*, **34**, 921 (1993).
13. G. Engelhardt, M. Urquidi-Macdonald M. and D. D. Macdonald, *Corros. Sci.*, **39**, 419 (1997).
14. D. D. Macdonald and M. Urquidi-Macdonald, *Corros. Sci.*, **32**, 51 (1991)
15. G. Engelhardt, M. Urquidi-Macdonald M. and D. D. Macdonald, *Corros. Sci.*, **41**, 2267 (1999).



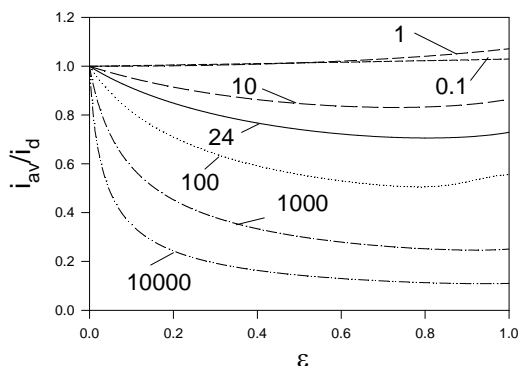
**Figure 1.** Concentration of ions of corroding metal under diffusion control and under steady-state periodic loading conditions as a function of the distance,  $y$ , [see Equation (16)] for different lengths of the corroding crack.  $C_0 = 0.01$  M,  $C_s = 1$  M,  $D_I = 10^{-5}$  cm<sup>2</sup>/s,  $f = 1$  Hz,  $\varepsilon = 0.2$ .



**Figure 2.** Ratio of the averaged limiting corrosion current density to the limiting corrosion current density calculated in the absence of advection as a function of dimensionless frequency at different values of parameter  $\varepsilon$ . The dashed lines represent the asymptotic solutions (for  $f^* \rightarrow \infty$ ) [see Equation (21)].



**Figure 3.** Concentration of ions of corroding metal under steady-state periodic loading conditions as a function of the distance,  $y$ , [see Equation (12)] for different lengths of the corroding crack.  $C_0 = 0.01$  M,  $C_s = 1$  M,  $D_1 = 0.72 \times 10^{-5}$  cm<sup>2</sup>/s,  $D_2 = 2.032 \times 10^{-5}$  cm<sup>2</sup>/s,  $f = 1$  Hz,  $\varepsilon = 0.2$ ,  $\alpha = 1$ ,  $i_m = 10^{-3}$  A/cm<sup>2</sup>.



**Figure 4.** Ratio of the averaged (over the period of oscillation) corrosion current density in the case of corrosion fatigue to the corrosion current density at the absence of advection as a function of parameter  $\varepsilon$  for different values of parameter  $A$ . The value  $A = 24$  corresponds to values of parameters that can be found in captures to the Figures 1 and 3.