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A mathematical model for crevice corrosion under porous deposits

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ABSTRACT

A model has been developed to investigate the corrosion of steels in a thin, narrow crevice formed between the metal surface and an oxygen-permeable, porous deposit. A thin electrolyte layer exists within the deposit, due to geochemical fluids dripping onto a deposit-covered surface or due to the adsorption of moisture by a hygroscopic deposit. Mass transfer by diffusion and ion migration is considered in both the electrolyte films inside and outside of the crevice. The main reactions considered are the anodic dissolution of the alloy substrate, hydrolysis of the alloying element cations, dissociation of water, and the cathodic reduction of oxygen, hydrogen ion, and water. Special attention has been given to the role of parameters connected with the porous layer (porosity, tortuosity, and the layer thickness) on the rate of crevice corrosion. It is shown that the cavity acts as an 'electrochemical amplifier' from the point of view of the concentration of aggressive anions that leads to increasing of corrosion rate and to a higher probability of pit nucleation within the crevice.

1. Introduction

Very often, metal surfaces that are exposed to moist, ambient air become covered with thin layers of water that contain oxygen, ionic species, corrosion products, and solid deposits (e.g., dust). These species may originate from the water source (e.g., calcareous deposits), dissolution of gases, dissolution of extraneous deposits (e.g., dust), including hydroscopic salts, and corrosion products [1,2]. Localized corrosion in the form of pits may initiate on a free metal surface, if the metal potential is sufficiently high and the environmental conditions are sufficiently aggressive [3]. Precipitates, metal oxides scales, as well as geometrical crevices can generate occluded local geometries that trap electrolytes and thus promote localized corrosion, such as pitting or crevice corrosion [2,3]. One special case of corrosion in occluded regions is the corrosion under a porous dust deposit that can be considered as a permeable membrane for oxygen (see Fig. 1).

As reported in the literature, many studies have been reported on modeling of the concentrations and potential distribution in long narrow crevices, see, for example Refs. [4,5]. The review of some of the latest works can be found in Ref. [6]. However, it is impossible to directly transfer the results of these models to the case of corrosion under oxygen-permeable, porous layers. The main reason is that, due to the depletion of oxygen in the entry region of the crevice, it is possible to neglect oxygen reduction inside the crevice and this assumption is made in the overwhelming majority of the studies devoted to the classical crevice corrosion. On the other hand, it is obvious that the quantitative description of corrosion in systems of the type under study is impossible without taking into account oxygen reduction inside the crevice with oxygen being continually supplied through the permeable wall.

The problem of corrosion under porous media has also been considered in connection with coating systems. Thus, Song et al. [7] developed a model to investigate the corrosion of a coated pipeline surface in a thin, narrow crevice formed between the pipe surface and the coating. The crevice forms when a holiday exists in the coating and when coating disbonds from the pipe surface. Taken alone, this model is rather simplistic (but nevertheless important), because it considers only the transport of oxygen and current flow in accordance with Ohm's law inside the crevice.

It is also important to note that, in the great majority of the papers devoted to the problem of mass and charge transfer in localized corrosion, it is tacitly assumed that in the case of a sufficiently deep pit or crevice, it is possible to neglect the potential drop in the external environment (outside the pit or crevice) and calculate the potential distribution by solving the balance equations only in the internal environment (inside the pit or crevice). However, as we have previously shown in the development of various 'coupled environment' models for stress corrosion cracking (coupled environment fracture model, CEFM [8,9]), pitting corrosion (coupled environment pitting model, CEPM [9] and corrosion fatigue (coupled environment corrosion fatigue model, CECFM [9] it can be shown that such a simplification can lead to substantial errors (especially in the case of dilute electrolytes) and the potential drop in the system can be found only by solving the transport

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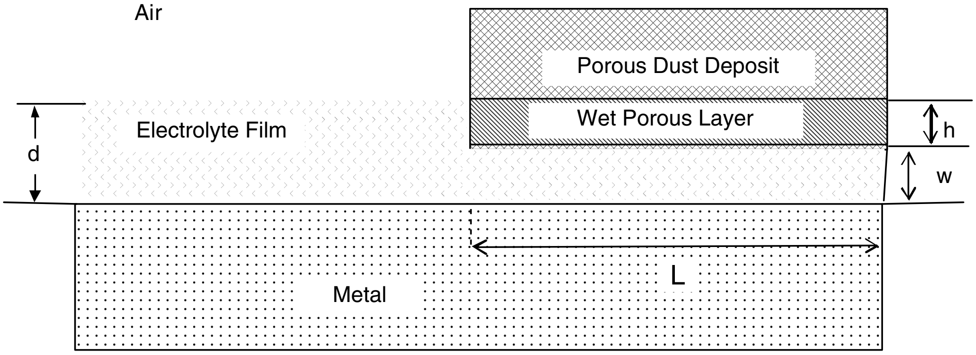

Fig. 1. Geometry for crevice corrosion under an oxygen-permeable deposit.

and potential distribution equations for the coupled internal and external environments simultaneously with the viable physical solution being that which conserves charge in the system (i.e. it assumed that the current that flows outside the cavity is consumed on the external passive surface). However, in these past studies, it has been assumed that, due to efficient mixing of the electrolyte, no concentration gradients exist outside the crevice and potential distribution in the external environment can be found as the solution of Laplace's equation for the electrostatic potential. It is clear that such a simplification can not been applied to the case when a thin electrolyte film (having a thickness of the order of micrometers) covers the external metal surface. In this case, the full set of mass transfer equations must be solved simultaneously inside and outside of the cavity, in order to obtain concentrations and potential distributions in the system.

Accordingly, the purpose of this paper is to develop a mathematical model that explores the behavior of crevices with walls that are permeable to oxygen.

2. Mathematical model

It has been previously suggested that, in the mathematical simulation of the corrosion of steels in neutral solutions, at least six species in the solution must be taken into account [10]. These species are the metal (e.g. Fe) ions from the dissolution process, sodium and chloride ions (for example), which are commonly included to control the bulk conductivity, hydrogen and hydroxyl ions from the dissociation of water, and a metal hydrolysis product [e.g. $Fe(OH)^+$]. For the current investigation, it is necessary to assume that dissolved oxygen is also present in the solution and, accordingly, it is assumed that there are seven different species, S_k, inside and outside the cavity

$$S_1 = Me^{2+}, \quad S_2 = M(OH)^+, \quad S_3 = Na^+, \quad S_4 = Cl^-,$$
$$S_5 = H^+, \quad S_6 = OH^-, \quad S_7 = O_2$$

with the volume-based concentrations being designated as, C_k (mol/cm^3), k = 1, 2,. . .,7.

It is also assumed, for simplicity, that alloy dissolution can be simulated by the dissolution of a single metal, Me, having an effective (composition-averaged) valence z (instead of the actual dissolution parameters for the alloy components) and an effective, composition-averaged atomic weight, A. Accordingly, dissolution of the alloy in the active or passive region is represented as

$$Me - Me^{z+} + ze \tag{1}$$

In this article, in order to be specific, we assume that z = 2, but in the general case z does not have to be integer number. Thus, for Alloy C-22 (nominal composition in atomic percent: Ni56Cr22Mo13), z = 2.15 as calculated from the composition and the common oxidation states of the components [11].

The cathodic reduction of oxygen, hydrogen ion, and water i.e.

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \tag{2}$$
$$H^+ + e \rightarrow (1/2)H_2 \tag{3}$$

and

$$H_2O + e \rightarrow OH^- + (1/2)H_2 \tag{4}$$

respectively, are also assumed to take place on the alloy surface within the crevice and on the alloy surface external to the crevice.

Additionally, three homogeneous reactions are presumed to occur in the system

$$Me^{2+} + H_2O = Me(OH)^+ + H^+ \tag{5}$$
$$Me(OH)^+ + H_2O = Me(OH)_2(s) + H^+ \tag{6}$$

and

$$H_2O = H^+ + OH^- \tag{7}$$

These reactions describe metal ion hydrolysis (Reaction (5)), hydrolysis product solubility/hydroxide precipitation (Reaction (6)), and the dissociation of water (Reaction (7)). Reaction (6) also limits the concentrations of metal species in the film and in the cavity via precipitation.

We will also assume that the width of electrolyte film, d, the width of the crevice, w, (which can be a function of the coordinate along the metal surface, x) are much smaller than the crevice depth. L, i.e.

$$d, w << L \tag{8}$$

In this case, under steady-state conditions, the mass transfer equations are of the form

$$\frac{d(wN_k)}{dx} = wR_{Vk} + N_{sk,1} + N_{sk,2}, \quad k = 1, \ldots, 7 \tag{9}$$

where N_k is the ionic flux density, x is the distance down the crevice (x = 0 corresponds to the crevice mouth), R_{Vk} is the rate of creation of ionic species k per unit volume, $N_{sk,1}$ and $N_{sk,2}$ are the fluxes of species k at the metal/solution interface and solution/air interface outside the crevice or at the solution/deposit interface inside the crevice, and w is the width of the crevice at $x \geqslant 0$ (inside the crevice) and the width of the electrolyte film for $x < 0$ (outside the crevice).

According to dilute solution theory, the molar flux of species, k, is given by the Nernst–Plank equation

$$N_k = -D_k\left(\frac{dC_k}{dx} + \frac{z_kF}{RT}C_k\frac{d\varphi}{dx}\right), \quad k = 1, \ldots, 7 \tag{10}$$

where D_k is the diffusion coefficient and z_k is the charge, T is the temperature, R is the gas constant, and φ is the electrostatic potential in the solution. We further assume that C_k and φ are averaged across the width of electrolyte film inside and outside the cavity. The solution is taken to be electrically neutral, so that

$$\sum_k z_k C_k = 0 \tag{11}$$

The fluxes of species, k, at the metal–solution interface on the side walls, $N_{Sk,1}$ are expressed as

$$N_{S1} = \frac{i_P}{2F}, \quad N_{S2} = N_{S3} = N_{S4} = 0, \quad N_{S5} = -\frac{i_{H^+}}{F},$$
$$N_{S6} = \frac{i_{OH^-}}{F}, \quad N_{S7} = -\frac{i_{O_2}}{4F} \tag{12}$$

where i_P is the *passive* corrosion current density (which is assumed to be independent of potential) and partial currents for Reactions (2)–(4) are described by Tafel's equation

$$i_{H^+} = A_1 C_5 \exp\left[-\frac{\alpha_1 FE}{RT}\right] \tag{13}$$

$$i_{OH^-} = A_2 \exp\left[-\frac{\alpha_2 FE}{RT}\right] \tag{14}$$

and

$$i_{O_2} = A_3 C_7 \exp\left[-\frac{\alpha_3 FE}{RT}\right] \tag{15}$$

where α_1, α_2, and α_3 are transfer coefficients, E is the local electrode potential, C_5 and C_7 are the concentrations of H^+ and O_2, respectively, and A_1, A_2 and A_3 are constants that do not depend on potential. It is evident that, for points at the metal surface inside and outside the crevice, we have

$$E = E_{corr} - \varphi \tag{16}$$

where E_{corr} is the metal potential far away from the crevice mouth (at $x \to -\infty$).On the other hand, for the fluxes of species at the solution/air interface, $N_{Sk,2}$, are expressed as

$$N_{Sk,2} = 0 \quad \text{for } k \leqslant 6 \quad \text{and} \quad N_{Sk,7} = K(C_{7,b} - C_7, 6) \tag{17}$$

Here, it is assumed that flux density of the oxygen into the crevice is proportional to the concentration drop between the concentration of oxygen on the outer side of the wet part of the porous deposit, $C_{7,b}$ (this concentration can be estimated via Henry's law), and the local value of the oxygen concentration, C_7. The permeability coefficient, K, can be presented in the form

$$K = \frac{\varepsilon}{\tau^2}\frac{D_7}{h} \tag{18}$$

where ε is the porosity, τ is the tortuosity and h is the width of the wet part of the porous deposit. Eq. (17) can be formally used also outside the crevice assuming that K is sufficiently large number ($K \to \infty$) which is equal to $C_7 = C_{7,b}$.

In accordance with general rules, the homogeneous terms, R_{Vk}, in balance equations can be written as

$$R_k = \sum_{m=1}^{M}\left[-r_m v_{km}\left\{\prod_{v_{km}>0} C_k^{v_{km}} - K_m \prod_{v_{km}<0} C_k^{-v_{km}}\right\}\right] \tag{19}$$

where r_m is an adjustable numerical rate parameter for Reaction m ($m = 1,2,\ldots,M$), K_m is the equilibrium constant for Reaction m, and v_{km} is the stoichiometric coefficient for species k in mth chemical reaction. If the rates of the chemical reactions are sufficiently high, the concentrations of the species can be set equal to their equilibrium values with the equilibrium constants K_1, K_2, and K_w being defined as

$$K_1 = C_2 C_5 / C_1, \quad K_2 = C_5 / C_2, \quad \text{and} \quad K_w = C_5 C_6 \tag{20}$$

where the activity coefficients are assumed to be unity, as are the standard state concentrations. This may or not may be a good assumption, depending upon the ionic strength.The boundary conditions far from the crevice mouth (at $x \to -\infty$) are written as

$$C_5 = 10^{-pH_b-3}, \quad C_6 = \frac{K_w}{C_5}, \quad C_2 = \frac{C_5}{K_2}, \quad C_1 = \frac{C_2 C_5}{K_1}, \quad C_3 = C_{NaCl,b},$$
$$C_4 = 2C_1 + C_2 + C_3 + C_5 - C_6, \quad C_7 = C_{O_2,b}\varphi = 0 \quad \text{at } x \to \infty \tag{21}$$

where pH_b is the bulk value of the pH and $C_{NaCl,b}$ and $C_{7,b}$ are the bulk concentrations of NaCl and O_2, respectively. These quantities are presumed to be known.

At the crevice tip, the boundary conditions are obvious

$$\frac{dC_k}{dx} = 0 \quad \text{at} \quad k = 1, 2, \ldots, 7 \tag{22}$$

2.1. Numerical solution

The system of nonlinear mass transfer Eqs. (9)–(11) were linearized by using the standard technique (see, for example, Ref. [12]) and at each iterative step the resulting system of ordinary differential equations was solved by using the finite difference method. The linear system of equations is solved by using the Thomas algorithm for block tridiagonal matrixes [12,13]. After finding the solution, C_k, it is declared to be $C_{k,old}$ and the iteration is continued until satisfactory convergence is achieved. To insure convergence of this algorithm, each flux on the metal/electrolyte interface, $N_{Sk,1}$, was multiplied by a factor, f. Initially, f was chosen to be 10^{-7}, and on each step of the iteration f was increased by a factor 1.05 until f became equal to 1. In some cases, in order to insure convergence, it was necessary to use, additionally, the method of lower relaxation. This is enacted by noting that after each solution of the system of equations, new values of C_k are recalculated via the relation

$$C_k = \alpha C_k - (1 - \alpha) C_{k,old} \tag{23}$$

where $\alpha < 1$ is the relaxation parameter. These measures were necessary, because the equations are extraordinarily stiff.

3. Results and discussion

Typical examples of the concentration and potential distributions that were obtained using parameters from Table 1 are shown in Figs. 2 and 3.

It is assumed that the rates of chemical reactions (parameters r_m) are high enough that chemical reactions (5)–(7) can be considered

Table 1
Parameters used in the calculations

Thermodynamic data	Kinetic data
$K_1 = 10^{-9.8}$ mol/L	$A_1 = 2 \times 10^3$ A mol^{-1} cm
$K_2 = 10^{-4.9}$ mol/L	$A_2 = 0.8 \times 10^{-7}$ A/cm^2
$K_W = 10^{-13.98}$ (mol/L)^2	$A_3 = 1.62 \times 10^3$ A mol^{-1} cm
Diffusion coefficients	$\alpha_1 = 0.5$
Me^{z+} $D_1 = 0.72 \times 10^{-5}$ cm^2/s	$\alpha_2 = 0.5$
$Me(OH)^+$ $D_2 = 1.0 \times 10^{-5}$ cm^2/s	$\alpha_3 = 0.5$
Na^+ $D_3 = 1.334 \times 10^{-5}$ cm^2/s	*Geometrical parameters*
Cl^- $D_4 = 2.032 \times 10^{-5}$ cm^2/s	$w = 10^{-3}$ cm
H^+ $D_5 = 9.302 \times 10^{-5}$ cm^2/s	$d = 1.5 \times 10^{-3}$ cm
OH^- $D_6 = 5.3 \times 10^{-5}$ cm^2/s	$L = 1$ cm
O_2 $D_7 = 2.29 \times 10^{-5}$ cm^2/s	*Temperature*
Solution data	$T = 25$ °C
$C_{NaCl,b} = 0.1$ mol/L	
$pH_b = 8$	
$C_{7,b} = 0.229 \times 10^{-3}$ mol/L	

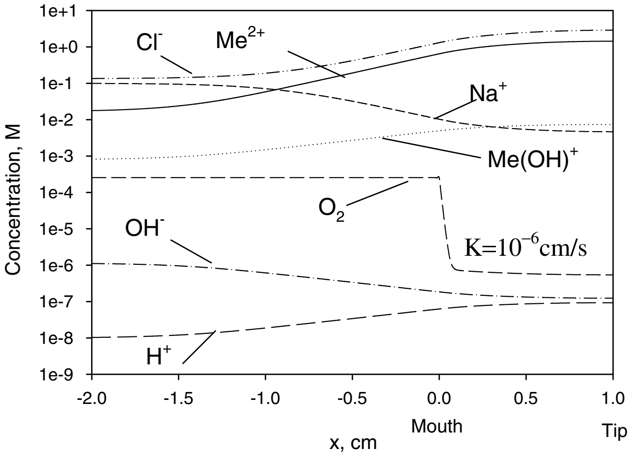

Fig. 2. Calculated averaged concentrations of species inside ($x > 0$) and outside ($x < 0$) of the crevice. Permeability coefficient for the transfer of oxygen through the porous wall = 10^{-6} cm/s. Parameter values are given in Table 1.

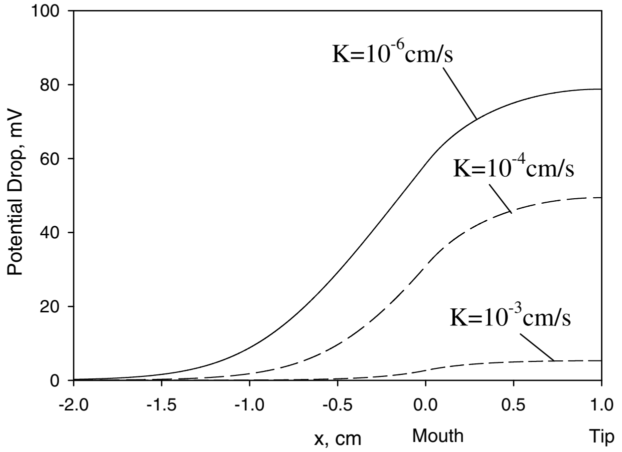

Fig. 4. Calculated averaged potential drop inside ($x > 0$) and outside ($x < 0$) a crevice for permeability coefficients for the transfer of oxygen through the porous wall, K. Parameter values are given in Table 1.

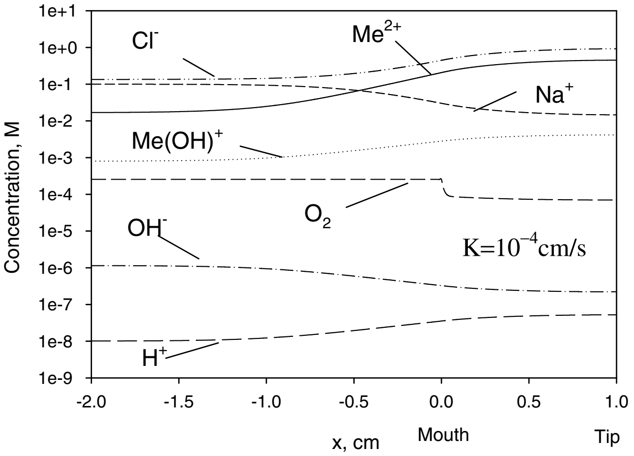

Fig. 3. Calculated averaged concentrations of species inside ($x > 0$) and outside ($x < 0$) a crevice. Permeability coefficient for the transfer of oxygen through the porous wall = 10^{-4} cm/s. Parameter values are given in Table 1.

to be at equilibrium. All thermodynamic and kinetic data (corresponding to the corrosion of carbon steel in chloride solutions) are taken from Ref. [10] except for the kinetic parameters for oxygen reduction, which were taken from Ref. [14].

The corresponding potential drop relative to a point far away from the crevice mouth can be found in Fig. 4.

These figures show that the effect of the wall porosity increases with decreasing permeability coefficient, K. For given values of the various parameters summarized in Table 1, the porous layer practically can be considered as being non-permeable for $K = 10^{-6}$ cm/s and the system reverts to a classical crevice. Thus, for $K < 10^{-6}$ cm/s, the concentration and potential distributions from Figs. 2–4 practically do not differ from the corresponding distributions calculated within the framework of classical crevice corrosion with one inert wall in place of the porous wall. In the opposite case of a high values for K (at $K > 10^{-2}$ cm/s for the given values of parameters), corresponding to a highly permeable wall (deposit), it is possible to simply ignore the existence of the porous layer.

Generally speaking, on the basis of similar calculations, it becomes possible to estimate the conditions (chloride concentration, pH, and potential drop) inside a crevice with porous walls and, accordingly, to predict the critical values of the mass conductivity coefficient, K_{cr}. The latter parameter can be defined from the conditions that for $K < K_{cr}$ some critical conditions can be distinguished corresponding to the initiation of crevice corrosion. Such conditions are different for different metal/electrolyte systems. Thus, a critical condition might correspond, for example, to increasing the chloride concentration inside the crevice over some threshold limit [15], at which point crevice corrosion would initiate. However, in any case, if the value of K_{cr} is determined, and some data on the properties of the porous layer (porosity, tortuosity) are available, it becomes possible to estimate the critical width of the wet part of the porous deposit, h_{cr}, above which the crevice would become active. The value of h_{cr} is determined from the condition that at $h > h_{cr}$ crevice corrosion occurs. As follows from Eq. (18), h_{cr} can be estimated as

$$h_{cr} = \frac{\varepsilon}{\tau^2}\frac{D_7}{K_{cr}} \tag{24}$$

The value of the ratio ε/τ^2 that describes the reduction of diffusion coefficient in the porous media can differ by orders of magnitude for different systems from ≈ 1 to very small numbers. Thus, in Ref. [10], the impact of reducing the diffusivities of all species in a porous medium by a factor of 10^4, due to porosity and tortuosity, on specie distributions in the crevice was considered. If, for example, the critical value of K is 10^{-4} cm/s and $\varepsilon/\tau^2 = 0.01$, Eq. (24) yields $h_{cr} \approx 2 \times 10^{-3}$ cm. If we know the growth rate of the porous layer, and its appropriate properties (porosity, tortuosity), the above condition allows us to estimate the critical time for initiation of crevice corrosion.

It is evident that the influence of the porous deposit on the conditions inside the crevice is different for different systems. Thus, Figs. 5 and 6 illustrate the influence of the mass conductivity of the porous wall on the potential drop at the tip of the crevice relative to a point far away from the crevice mouth, $\Delta\varphi$, for different values of the passive corrosion current density, i_p, and the width of the crevice, w. As might be expected, the influence of the porous layer decreases with a decrease of the passive corrosion current density and with an increase of the width of the crevice. The corresponding increase in the chloride concentration (amplifier properties of the crevice) can be found from the data in Figs. 5 and 6, by using Boltzmann's distribution

$$\frac{C_4}{C_{4,b}} = \exp\left(\frac{F\Delta\varphi}{RT}\right) \tag{25}$$

The work reported here also shows that, in describing quantitatively the conditions that exist inside corroding crevices with permeable and non-permeable walls, and that open to a thin electrolyte film that exists on the external surfaces, it is absolutely essential to include the concentration and potential distributions in the external environment (outside of the crevice). This is the basis of the various "coupled environment" models for localized corrosion that have been developed over the past decade or so. These models couple the potential distributions in the internal and external environments by requiring that a common potential exists at the crevice mouth and charge is conserved globally in the system. The latter condition ensures that the solution is physically real [8]. In the present case, the importance of external environment is illustrated by the data plotted in Fig. 3. Thus, Fig. 4 clearly shows that, for the given values of the various parameters in the model, more than 75% of potential drop in the system occurs in the external environment.

As is also shown in Figs. 2 and 3, the concentrations of the principal species that determine the conductivity of electrolytes (Me^{2+}, Na^+ and Cl^-) can differ by orders of magnitude outside the crevice and, accordingly, the conductivity of the film also can differ by orders of magnitude. In turn, this means that prediction of the potential distribution along a metal surface covered with a thin electrolyte films must be done, in the general case, by solving the full system of mass transfer equations together with the local electroneutrality condition. However, the majority of the studies that attempt to quantitatively describe corrosion in such systems, (for example, in the field of atmospheric corrosion) attempt to solve Laplace's equations (i.e. to apply Ohm's law) and this can lead, in some cases, to significant error.

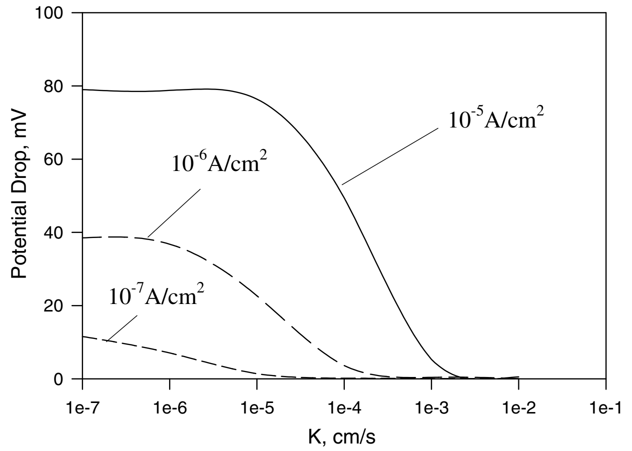

Fig. 5. Calculated averaged potential drop at the tip of the crevice relative to a point far away from the crevice mouth as a function of permeability coefficient for the different values of the passive corrosion current density. Other parameter values are given in Table 1.

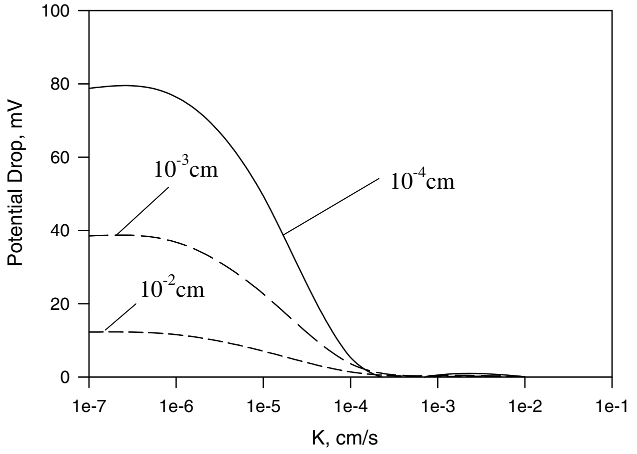

Fig. 6. Calculated averaged potential drop at the tip of the crevice relative to the point far away from the crevice mouth as a function of the permeability coefficient for the different values of the crevice width, *w*. The width of the electrolyte film outside of the crevice, *d*, equals 1.5*w*. Other parameter values are given in Table 1.

4. Conclusion

A mathematical model for estimating concentration and potential distributions inside and outside crevices with porous walls that are permeable to oxygen penetration and that are open to a thin electrolyte film on the external surface has been developed. The model is based on the solution of the system of mass transfer equations along with the equation of electroneutrality in a one dimensional approximation. The governing mass transfer equations were kept in rate format (i.e. chemical terms were used in normal form without eliminating the chemical terms by adding and subtracting the mass balance equations), which allows generalization of the computer code to the case of an arbitrary number of chemical and electrochemical reactions. A special relaxation procedure has been used to ensure the convergence of the solution in the presence of very fast chemical reactions. The model can be used to describe many technological problems (for example, corrosion of a coated pipeline surface in a thin, narrow channel crevice formed between the pipe surface and a disbanded coating) and atmospheric corrosion.

Calculations show that the effect of a porous layer increases with decreasing mass permeability, *K*. For some particular sets of parameters, the critical values of the permeability coefficient for inactivation of the crevice, K_{cr}, has been estimated. The K_{cr} value can be defined from the conditions that at $K < K_{cr}$ some critical conditions can be distinguished and the crevice corrosion can be initiated. It has been shown that the influence of the porous layer is lowered by decreasing the passive corrosion current density and increasing the width of the crevice.

It has been shown that, by quantitatively describing the conditions that exist within a corroding crevice with permeable and non-permeable walls, and which opens to a thin electrolyte film on the external surface, it is absolutely impossible to neglect the concentration and potential drops in the external environment (outside the crevice). In conventional modeling of crevice corrosion, the models calculate the potential distribution by solving the balance equations only for the internal environment (inside the crevice), with the exception being the various 'coupled'. Prediction of the potential distribution along a metal surface that is covered with a thin electrolyte films must be done, in the general case, on the basis of solving the full system of mass transfer equations, together with the electroneutrality condition, not on the basis of Laplace's equation.

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