



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Corrosion Science 46 (2004) 1159–1187

**CORROSION
SCIENCE**

www.elsevier.com/locate/corsci

Estimation of corrosion cavity growth rate for predicting system service life

George Engelhardt ^a, Digby D. Macdonald ^{b,*}

^a *OLI Systems Inc., 108 American Road, Morris Plains, NJ 07950, USA*

^b *Center for Electrochemical Science and Technology, The Pennsylvania State University,
201 Steidle Building, University Park, PA 16802-5006, USA*

Received 9 April 2003; accepted 26 September 2003

Abstract

It has been shown that under real, practical conditions, values of the critical pit depth of the system, x_{cr} , and typical service life, t_s , impose significant restrictions on the corrosion current densities (averaged and initial) and thus on the potential and concentration drops that might be observed in the corrosion cavity. Thus, it is shown that, if x_{cr} does not exceed the order of 1–10 mm, and if the order of t_s is not less than 1 year, initial corrosion current densities in real, open pits cannot exceed values of 10^{-4} – 10^{-3} A/cm², with the understanding that the polarization curve (corrosion current density vs. potential and the surface concentration of species) does not change as the pit propagates. Simple analytical expressions for predicting potential and concentration drops in open corrosion cavities, and for predicting cavity propagation rate in systems containing uni- and bi-valent anions in stagnant electrolytes under well-mixed, external conditions have been obtained. These expressions can be used to extrapolate the results of short-term corrosion experiment to future times. In particular, it is shown that, if localized corrosion takes place in an electrolyte having a conductivity of the order of that of seawater, it is possible to neglect the potential drop in an open corrosion cavity and hence to consider the rate of pit propagation as being constant under constant environmental conditions. The same conclusion holds for the pitting of 316 L steel, practically for any composition of the external electrolyte.

© 2003 Elsevier Ltd. All rights reserved.

* Corresponding author. Tel.: +1-814-863-7772; fax: +1-814-863-4718.

E-mail address: ddm2@psu.edu (D.D. Macdonald).

1. Introduction

In the case when localized corrosion cannot be prevented, it becomes very important to predict the propagation of corrosion damage in order to assess the risk of failure. It is evident that a principal theoretical problem in predicting damage due to localized corrosion lies in estimating the dimensions of the cavity at any given time as a function of the parameters controlling the corrosion process, such as the corrosion potential of the metal, E_{corr} , composition of the bulk electrolyte, fluid velocity, temperature, etc. This problem reduces to one of calculating the corrosion current density, i_{corr} , on the electrode (corrosion cavity) surface and applying Faraday's law to yield the velocity of the dissolving metal surface $\vec{V}_s = K_V i_{\text{corr}} \vec{n}$, where K_V is the electrochemical equivalent, and \vec{n} is the unit vector pointed normally from the solution to the metal interface.

In turn, it is assumed that i_{corr} is determined by the local values of the metal potential, E , and solute concentrations, C_{ks} , at the active surface. Here, the index "s" refers all values to the electrode surface and index $k = 1, 2, \dots, N$ denotes species in the solution. However, in the general case, the values of E and C_{ks} can be significantly different from the corrosion potential of the metal, E_{corr} , and the bulk concentration of the species, $C_{k\infty}$, (index " ∞ " refers all values to the bulk), respectively, i.e. from the values that are known from experiment. The unknown values of E and C_{ks} can be found by solving the system of transport equations, as described in numerous reviews and papers, in which the problem of modeling mass and charge transfer inside and outside of corrosion cavities is discussed (see, for example, Refs. [1–26]).

Generally speaking, the quantitative description of transport processes is a very complicated task, especially for systems involving migration, homogeneous chemical reactions, and complicated (and sometimes unknown) geometries. Accordingly, it would be remarkable if preliminary analysis was to show that, for some particular systems, no significant potential or concentration drops exist within an active corrosion cavity. It is evident that quantitative prediction of the propagation of corrosion damage in such systems would be greatly simplified. In particular, if the external conditions (corrosion potential, composition of bulk electrolyte, hydrodynamic conditions) and the polarization curve (corrosion current density vs. potential and the surface concentrations of species) do not change with time, a constant propagation rate is expected.

In the papers cited above, significant potential and concentration drops have been predicted to exist in corrosion cavities. However, in the majority of these papers, no attempt was made to predict the shape of the growing cavity for times that are typical of practical system (>1 year). In many cases, the results can be applied only to the initial stage of pit propagation, and, very often, the calculations were made for metal potentials that are considerably higher than the free corrosion potential that is normally observed in a real system.

It can be shown that, in many practical systems, the average current density that is estimated from the dimensions of the corrosion cavity is normally much lower than the current densities considered in the cited articles. In many cases, the value of the corrosion current must be so low that it is possible to neglect the influence of the

potential drop inside the pit on the cavity propagation rate. Accordingly, the cavity propagation rate can be regarded as being constant if the corrosion current density depends only on the metal potential. This article is devoted to examining the conditions under which it is possible to use this simplification.

For simplicity, only the case where metal dissolution is the only electrochemical process in the corrosion cavity, and where the surface outside of corrosion pit is insulated, will be considered; i.e. we will neglect any cathodic reactions that may take place inside or outside the pit. However, it is clear that any cathodic reaction that occurs within the cavity can only decrease the absolute value of the coupling current density and hence would further reduce the potential drop in the system. In other words, our analysis will yield the upper limit for potential drop, and if this is found to be insignificant under the simplified conditions, it should be even less significant in the real system.

We must however emphasize that all results will be applicable only for the case of an open cavity under transport conditions that are not significantly more severe than the transport conditions that exist in an open, hemispherical pit. It is clear that in closed cavities, mass and charge transfer may be so limited that significant potential drops will be observed, even for very low current densities. The same limitations can also occur (and hence the theory developed in this work will be inapplicable) for the case of bottle-shaped cavities [27], which simply represent a type of closed pit, for corrosion under very thin electrolyte films, for corrosion in the presence of gas bubbles [28], corrosion under porous deposits, and for other factors that reduce communication between the cavity internal and external environments.

2. Estimation of concentration drops in real corrosion cavities

The size of pits that give rise to dangerous conditions in technological applications can vary over a very wide range—from micropits ($\sim 1\text{--}100\ \mu\text{m}$), that may lead to failure of coatings, thin membranes, electronic films, etc., and that may result in the nucleation of corrosion cracks, up to large corrosion cavities ($\sim 1\text{--}10\ \text{mm}$), that lead to the perforation of container walls, for example [22]. Let us denote by t_s the service life of a particular system, i.e. the time at which the depth of the pit, x , reaches some critical value, x_{cr} . Generally speaking, corrosion is a slow process, and for most practical systems the service life is of the order of 1–100 years. If the failure of the system occurs before one year, we will stipulate “immediate failure” and no prediction of damage is necessary. Here, we define “failure” as being that observation time at which the depth of the greatest pit exceeds the critical dimension, x_{cr} , for example the thickness of the metal wall.

The latter assumption implies some restrictions under which corrosion damage can propagate in real systems. Thus, for example, it was shown that micropits that form on Type 304 SS in acidic NaCl solution can propagate only if the condition

$$xi \geq (xi)_{\text{cr}}, \quad (1)$$

holds with the value of $(xi)_{\text{cr}}$ being $0.3 \times 10^{-2}\ \text{A/cm}$ [29]. Letting

$$i = \frac{1}{K_V} \frac{dx}{dt}, \quad (2)$$

we obtain after integration of Eq. (1)

$$t_s \leq \frac{x_{cr}^2}{2(xi)_{cr} K_V}. \quad (3)$$

The value of the electrochemical equivalent volume, K_V can be estimated from the equation

$$K_V = \frac{\mu}{nF\rho}, \quad (4)$$

where μ is the molecular weight of the metal, n is the effective valence, ρ is the density, and F is Faraday's constant. For pure iron ($\mu = 55.847$ g/mol, $\rho = 7.874$ g/cm³), we estimate K_V to be 3.675×10^{-5} cm⁻³ C⁻¹. This means that, for example, a critical value $x_{cr} = 1$ mm is reached after 13 h from the initiation of corrosive attack and that $x_{cr} = 1$ cm is attained after 53 days. It is clear that such small values of the service life are not generally realized in real systems and hence Condition (1) is fulfilled only during the initial stage of pit propagation.

Condition (1) has the following physical meaning. It can be shown that the solutions to the coupled transport equations governing species concentrations and potential for the case of steady-state, non-convective electrolytic systems can be presented as functions of a single variable, the quasipotential, q , [30]. The quasipotential is a harmonic function, i.e. it satisfies Laplace's equation

$$\nabla^2 q = 0 \quad (5)$$

and satisfies the following boundary conditions:

$$q = 0, \quad (6)$$

far away from the electrode surface

$$\frac{\partial q}{\partial n} = 0, \quad (7)$$

at an insulating surface, and

$$\frac{\partial q}{\partial n} = i, \quad (8)$$

at the electrode surface.

For the case of a one-dimensional, deep cavity, the quasipotential at the pit bottom simply equals the product, xi , where x is the depth of the cavity. For the case of a hemispherical, open pit (see Fig. 1) the quasipotential near the electrode surface, can be presented in the form

$$q = axi, \quad (9)$$

where x is the radius of the hemisphere and the value of the dimensionless parameter, a , depends on the position on the electrode (pit) surface. It is assumed that the

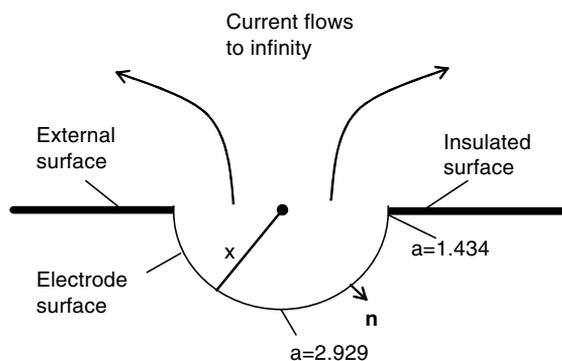


Fig. 1. Geometry of the hemispherical pit.

current density on the active surface, i , does not depend significantly on the surface coordinates (only under this condition is the development of a hemispherical pit possible). Numerical analysis reported in Ref. [31] shows that the parameter a increases from 1.434 at the pit edge to $2.929 \approx 3$ at the bottom of the pit. Consequently, Condition (1) implies that stable growth of a hemispherical pit is possible only if the concentration difference of the diffusing species between the interior surface of the pit and the bulk solution exceed some definite value. In accordance with calculations reported in Ref. [29], this critical value is approximately 3 M for the case of corrosion of Type 304 stainless steel in acidic NaCl solutions. However, as shown above, such a high value of the concentration drop cannot be realized in practical systems having a typical service life of many months or years.

Let us estimate the difference between the surface and bulk concentrations of dissolving metal ions, ΔC . Using Fick's Second Law, we have for a hemispherical pit

$$\frac{dx}{dt} = \frac{\mu j}{\rho} = \frac{\mu D \Delta C}{\rho x a}, \quad (10)$$

where j is the diffusion flux and D is the diffusion coefficient. If, during the whole process of pit propagation, the concentration difference increases above some critical value, ΔC_{cr} , this value must satisfy the following condition:

$$\Delta C_{cr} \leq \frac{a x_{cr}^2 \rho}{2 M D t_s}, \quad (11)$$

as is evident upon integrating Eq. (10). For example, if $t_s = 1$ year and $x_{cr} = 1$ mm, we have for the bottom of a hemispherical pit ($a = 3$), $\Delta C_{cr} = 0.66 \times 10^{-2}$ M, and for $t_s = 10$ years and $x_{cr} = 1$ cm we have $\Delta C \leq 0.66 \times 10^{-1}$ M (for $D = 10^{-5}$ cm²/s). It is important to note that Condition (11) is really an upper estimate, because migration and any chemical reactions that consume metal ion species can only reduce the value of ΔC_{cr} .

In our further quantitative analysis of this issue, we will always assume that $a \approx 3$, i.e. the calculations will refer to the bottom of a hemispherical pit. It is evident that, if the potential drop to the bottom of the pit (where it reaches a maximum) is not significant, it will be much less important for other points on the hemispherical surface. We can also state that the mere fact that hemispherical (or approximately hemispherical) pits exist can be explained by the insignificance of the potential drop in the corrosion cavity. Otherwise, the corrosion current density on the edge of the pit becomes higher than that on the bottom and the pit will quickly assume a shallow (“saucer”) form. It is worth noting that sufficiently deep pits ($x_{\text{cr}} \approx 1$ cm) very rarely have a shallow form with diameter being much larger than 1 cm. It is also worth noting that all equations developed in this article can be used for the case of a long, one-dimensional pit by simply letting $a = 1$.

Two important conclusions can be drawn from Eq. (11). Firstly, under real conditions, the difference between the surface and bulk concentrations of the dissolving species usually does not exceed 10^{-2} – 10^{-1} M and, accordingly, it would be very unusual that diffusion would control the pit propagation process (unless the solubility of corrosion products is very low). Secondly, due to the relatively low value of ΔC_{cr} , it is possible to use constant (bulk) values for the transport properties (diffusivity, mobility, etc.), when quantitatively describing transport processes in corrosion cavities.

It is also important to note that, in spite of the value of ΔC_{cr} being limited by Condition (11), the absolute value of ΔC_{cr} is much higher than the concentration of H^+ ions for corrosion in weakly acidic, neutral, or alkaline solutions. This means that the value of pH can change significantly at the bottom of the pit in comparison with the bulk value, in spite of the relatively low value of the corrosion current.

Finally, we now estimate the maximum value of the quasipotential, q , during the propagation of an open (hemispherical) pit. When a pit propagates at a constant velocity, $V = x_{\text{cr}}/t_s = K_V i_{\text{av}}$, we have

$$q_{\text{cr}} = ax_{\text{cr}}i_{\text{av}} = \frac{ax_{\text{cr}}^2}{K_V t_s}, \quad (12)$$

where i_{av} is the average corrosion current density over the service life. For $t_s = 1$ year and $x_{\text{cr}} = 1$ mm, we have $q_{\text{cr}} \approx 10^{-5}$ A/cm and for $t_s = 10$ years and $x_{\text{cr}} = 1$ cm we calculate $q_{\text{cr}} \approx 10^{-4}$ A/cm. Even for the extreme case of $t_s = 1$ year and $x_{\text{cr}} = 1$ cm, the value of q_{cr} is of the order of 10^{-3} A/cm. The value of q_{cr} can be regarded as an upper estimate of the quasipotential at $x = x_{\text{cr}}$, for the usual case when the pit propagation rate decreases with time, because a pit that reaches the assumed value of the critical depth, x_{cr} , will have a velocity that is less than the average velocity, x_{cr}/t_s , i.e. with $q < q_{\text{cr}}$. Here, we assume that the quasipotential at the pit bottom increases with pit growth (initially, at $t = 0$, $q = 0$). Of course, if the pit propagation rate increases with time, it must be that $q > q_{\text{cr}}$ at $t = t_s$. However, this means that the pit will propagate from a depth of $x = x_{\text{cr}}$ to $x = 2x_{\text{cr}}$ during a time that is significantly less than $t = t_s$. Clearly, such a situation is very difficult to imagine. Finally, we conclude that the value of 10^{-4} A/cm (and in extremely cases 10^{-3} A/cm) can be regarded as being limiting for the normal conditions of pitting corrosion.

3. Estimation of the potential drop in real corrosion cavities

For simplicity, we will estimate the potential drop in a cavity for the case when there is no convection or chemical reactions in the bulk of the solution under steady state conditions. We assume that, due to the modest value of the concentration drop in the solution, ΔC , it is not necessary to use the theory of concentrated solutions for describing mass transfer processes (see Ref. [23]) and, thus, the usual dilute solution theory can be applied. These assumptions lead to the following system of transport equations:

$$\nabla \cdot \vec{J}_k = 0, \quad k = 1, 2, \dots, N, \quad (13)$$

$$\vec{J}_k = -D_k \left(\nabla C_k + \frac{z_k F}{RT} C_k \nabla \phi \right), \quad k = 1, 2, \dots, N, \quad (14)$$

$$\sum_{k=1}^{k=N} z_k C_k = 0. \quad (15)$$

Here, C_k is the concentration of species k , N is the overall number of species in the solution, \vec{J}_k is the ionic flux density, D_k is the diffusion coefficient, which is assumed to be independent of concentration, z_k is the charge, T is the temperature, R is the gas constant, and ϕ is the electrostatic potential.

Let us assume that only one electrochemically active component (cation of the corroding metal), identified as $k = 1$, is present in the solution. Thus the concentrations of all other (inactive) species obey the Boltzmann distribution law (which follow from Eq. (14) and the condition that $\vec{J}_k = 0$), i.e.

$$C_k = C_{k\infty} \exp(-z_k F \phi / RT), \quad k = 2, 3, \dots, N, \quad (16)$$

Considering the condition of electroneutrality, one obtains for C_1

$$C_1 = -\frac{1}{z_1} \sum_{k=2}^N C_{k\infty} \exp(-z_k F \phi / RT). \quad (17)$$

Multiplying Eq. (14) by $z_k F D_1 / D_k$ and adding the results, and again considering the condition of electroneutrality, one obtains for the current density

$$\vec{i} = F \sum_{k=1}^N z_k \vec{J}_k = F z_1 \vec{J}_1 = -\kappa_{\text{eff}} \nabla \phi, \quad (18)$$

where the function

$$\kappa_{\text{eff}} = \frac{F^2 D_1}{RT} \sum_{k=1}^N z_k^2 C_k \quad (19)$$

is the “effective conductivity”. This quantity differs from the usual conductivity that is defined in dilute solution theory [32] by the replacement of all diffusion coefficients, D_k , by that for the electrochemically active component ($k = 1$) only. Since

$D_1 = D_1(C_1, C_2, \dots, C_N, T)$, introducing Eqs. (16) and (17) into Eq. (19) yields κ_{eff} as a function of potential ϕ :

$$\kappa_{\text{eff}}(\phi) = \frac{F^2}{RT} D_1(\phi) \sum_{k=2}^N C_{k\infty} (z_k^2 - z_1 z_k) \exp(-z_k F \phi / RT). \quad (20)$$

For the assumed conditions, the current density, \vec{i} , is proportional to the potential gradient only, although concentration gradients are also present in the solution. Substitution of Eq. (18) into the condition of charge conservation, $\nabla \cdot \vec{i} = 0$, yields the following equation for the potential:

$$\nabla \cdot (\kappa_{\text{eff}} \nabla \phi) = 0. \quad (21)$$

It is evident that, under the described conditions, the quasipotential, q , which satisfies Eqs. (5)–(8), can be defined by the relation

$$q = \int_0^\phi \kappa_{\text{eff}}(\phi) d\phi. \quad (22)$$

Because, as noted above, the concentration gradients in the corrosion cavity are not large, it is possible to neglect the concentration dependence of the diffusion coefficient D_1 to yield

$$q = F D_{1\infty} \sum_{k=2}^N C_{k\infty} (z_k - z_1) [1 - \exp(-z_k F \phi / RT)], \quad (23)$$

where $D_{1\infty}$ is the diffusion coefficient of the electrochemically active species in the bulk solution.

Eq. (23), or in the more general case, Eqs. (20) and (22), determine the value of the electrostatic potential, ϕ , as a function of the quasipotential, q . After numerical solution of these equations, it is possible to calculate the concentrations of all species by using Eqs. (16) and (17), thereby allowing one to estimate potential and concentrations drops in a corrosion cavity as a function of corrosion current density or cavity propagation rate. However it is possible also to obtain a simple, approximate (but accurate) analytical solution to Eq. (23). Under most real conditions, only negative species with charges of -1 or -2 are present in the solution. Let us denote their molar concentrations by C_1^- and C_1^{2-} respectively. Let us further introduce,

$$\delta_1 = C_1^- / C_{\text{t,an}} \quad \text{and} \quad \delta_2 = C_1^{2-} / C_{\text{t,an}}, \quad (24)$$

where $C_{\text{t,an}} = C_1^- + C_1^{2-}$ is the total molar concentration of anions in the solution. It is evident that $\delta_1 + \delta_2 = 1$. For high values of the electrostatic potential, ϕ , it is possible to neglect all terms containing $\exp(-z_k F \phi / RT)$ with $z_k > 0$, in Eq. (23). This means that, instead of a real electrolyte, which contains more than one type of cation, we consider an electrolyte containing a single cation—the cation of dissolving metal, which dominates the cation population near the electrode surface.

After this simplification, it is straight-forward to show that

$$\varphi = \frac{RT}{F} \text{Ln} \left[\frac{\sqrt{\delta_1^2(n+1)^2 + 4\delta_2(n+2)[\delta_2(n+2) + \delta_1(n+1) + q/q_0]} - \delta_1(n+1)}{2\delta_2(n+2)} \right], \quad (25)$$

where $q_0 = FD_1 C_{\text{tot}}^{\text{an}}$ and $n = z_1$. When the solution contains anions with one charge only (with absolute value of z), e.g. $\text{Cl}^- + \text{F}^-$ or $\text{SO}_4^{2-} + \text{CO}_3^{2-}$ but not $\text{Cl}^- + \text{SO}_4^{2-}$, Eq. (25) simplifies to

$$\varphi = \frac{RT}{zF} \text{Ln} \left[1 + \frac{q/q_0}{n+z} \right]. \quad (26)$$

Fig. 2 shows the applicability of the adopted approximations. Thus, for $q > 10^{-3}$, some discrepancy exists between the values of the potential calculated numerically from Eqs. (20) and (22) (i.e. by taking into account the concentration dependence of the diffusion coefficient) and that calculated numerically from Eq. (23), (i.e. at $D_1 = \text{const}$), but the difference is slight. The concentration dependence of D_1 was calculated by using the method described in Ref. [33] and by employing standard, commercial (OLI) software. We see that the concentration dependence of the diffusivity can play a visible role only for $q > 10^{-3}$ A/cm. Fig. 3 shows that, under these conditions, the Fe^{2+} concentration difference between the surface and bulk solutions, ΔC , reaches 0.7 M. However, as it was shown above, $q > 10^{-3}$ A/cm is normally not realized in freely corroding systems. The discrepancy between the values of potential

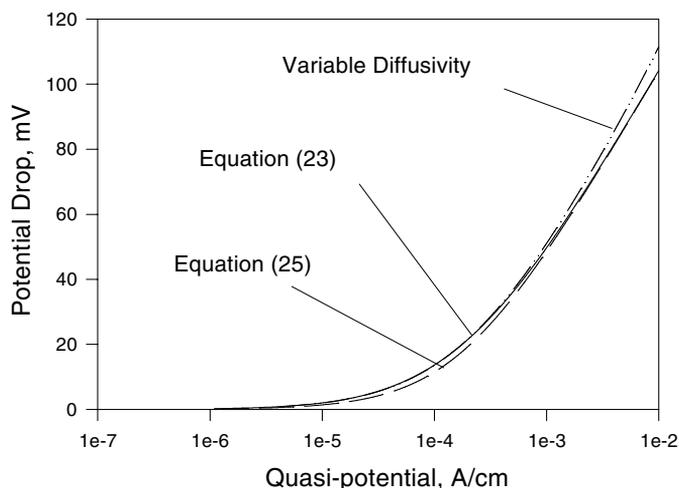


Fig. 2. The potential drop as a function of quasipotential for dissolution of iron in 0.1 M NaCl at $T = 25$ °C.

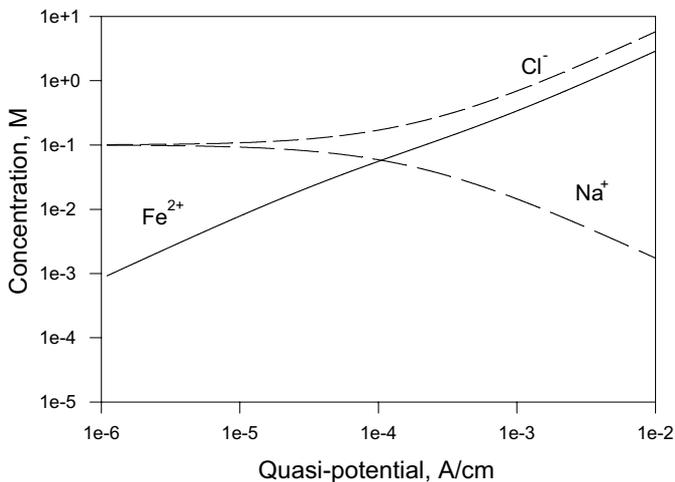


Fig. 3. Concentration of species as a function of quasipotential for the dissolution of iron in 0.1 M NaCl at $T = 25\text{ }^{\circ}\text{C}$.

calculated numerically from Eq. (23) and from the approximate analytical Expression (25) [which reduces to Eq. (26) with $z = 1$] does not exceed 2.25 mV and disappears completely for sufficiently large values of q .

Figs. 4 and 5 illustrate the sensitivity of the potential drop in a corrosion cavity to the nature of the corroding metal. We see that the potential drop is not very sensitive to the charge on the dissolving species, in the practical region of $q < 10^{-4}$. This is, because the nature of the bulk electrolyte defines the potential drop at low values of

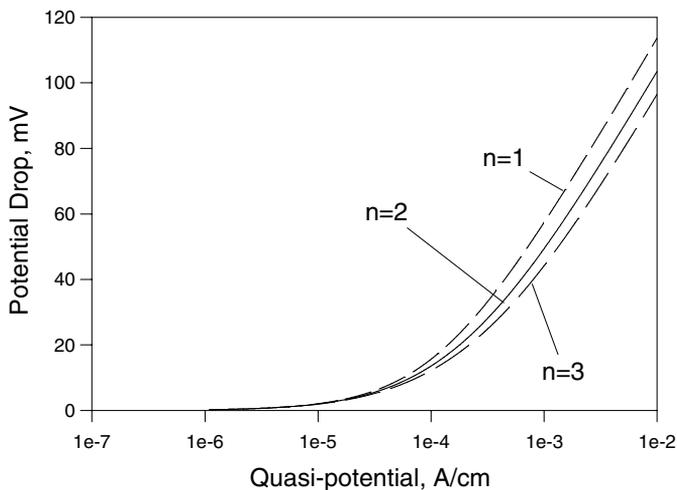


Fig. 4. The potential drop as a function of quasipotential for dissolution of hypothetical metals with different valence in 0.1 M NaCl at $T = 25\text{ }^{\circ}\text{C}$ and $D_{1\infty} = 0.614 \times 10^{-5}\text{ cm}^2/\text{s}$.

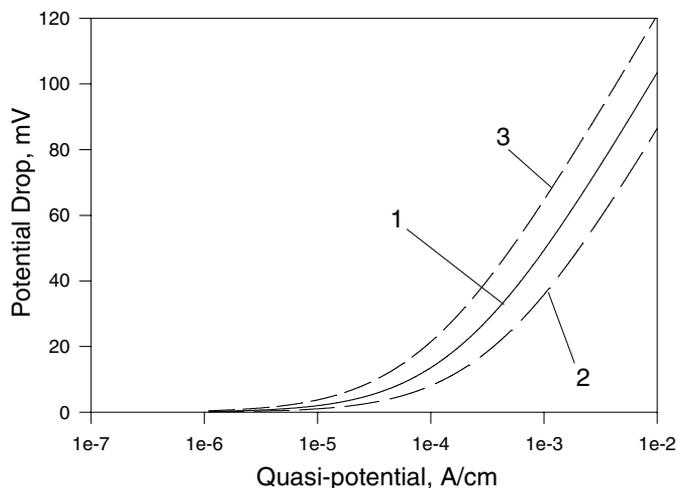


Fig. 5. The potential drop as a function of quasipotential for dissolution of hypothetical metals with $n = 2$ and different diffusivities $D_{1\infty} = D_0 = 0.614 \times 10^{-5} \text{ cm}^2/\text{s}$ (curve 1), $D_{1\infty} = 2 * D_0$ (curve 2), and $D_{1\infty} = 0.5 * D_0$ (curve 3) in 0.1 M NaCl at $T = 25 \text{ }^\circ\text{C}$.

ΔC . The sensitivity of the potential drop to the diffusivity of the dissolving species is more important. However, the value of the diffusion coefficient for Me^{n+} usually does not differ significantly for different metals.

It is evident that the most important parameter determining the dependence of the potential drop on quasipotential is the concentration of the bulk electrolyte, because the latter value can change by many orders of magnitude. Fig. 6 illustrates this dependence. We see that, if the concentration of NaCl is of (or exceeds) the order of that in sea water (0.5 M), the potential drop in the cavity does not exceed 4 mV, i.e. the potential drop can be regarded as being negligible in the practical region of quasipotential ($q \leq 10^{-4} \text{ A/cm}$). It is interesting to note that this conclusion can be made based only on the estimated concentration drop of the corroding species, ΔC , in the solution. Because the value of ΔC (0.66×10^{-2} – $0.66 \times 10^{-1} \text{ M}$) is an order of magnitude lower than the NaCl concentration in sea water (supporting electrolyte), it is possible to show that there is no significant potential drop in the cavity [32].

In the opposite case of tap water, there is no significant potential drop (less than 7 mV) when q does not exceed 10^{-5} A/cm . For example, this condition exists when the depth of the pit does not exceed 1 mm and the service life of the system exceeds 1 year.

It is interesting to note the intersection on the curves that correspond to tap water and to an electrolyte with a NaCl concentration of 0.1 M in Fig. 6. This can be explained by the influence of anions having a high absolute value of charge (SO_4^{2-} in our case). At sufficiently high values of the potential drop, these anions displace Cl^- from the electrode surface [see Eq. (16)]. Under these conditions, the limiting value of the potential drop (for sufficiently deep pits) is described by Eq. (26) with $z = 2$,

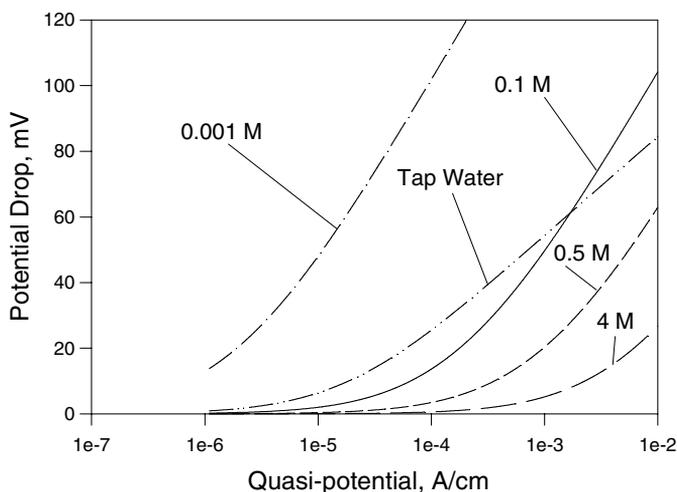


Fig. 6. The potential drop as a function of quasipotential for the dissolution of iron in electrolytes with different bulk concentration of NaCl at $T = 25^\circ\text{C}$. Model tap water has the following composition: $[\text{NaCl}] = 0.007\text{ M}$ and $[\text{Na}_2\text{SO}_4] = 0.054\text{ M}$.

whereas the limiting value of the potential drop in chloride solutions is described by the same equation with $z = 1$. In another words, the replacement of an anion with charge -1 by an anion of charge -2 reduces the potential drop in the solution by a factor of more than 2.

4. Estimation of the cavity depth as a function of time for real corrosion cavities

The relations obtained in the previous section allow us to estimate the potential (concentration) drop in an open corrosion cavity, if we know the dimensions of the cavity and the corrosion current density at the cavity surface. The latter value can be estimated on the basis of Faraday's law. However, it is not clear from the theory developed so far how significant the potential drop is in determining the cavity growth rate. A primary goal of this section is to explore this issue using the theory developed above.

For calculational purposes, under usual, practical corrosion conditions, we stipulate that the potential drop is not important if it is less than 5–10 mV. In the general case, we can judge the impact of the potential drop on the corrosion current density (pit propagation rate) only on the basis of the polarization curve. If, after substitution of the estimated value for ϕ_s into the polarization curve, the corrosion current density does not change significantly we can conclude that the potential does not influence on pit propagation rate. However, even in the case when ϕ_s has a significant impact on the corrosion current density, it does not necessarily mean that it significantly influences the pit depth as function of time. This is because, for example,

the drop in pit propagation rate may occur at the end of the observation period. That is why the most direct way to judge the importance of the potential drops in the cavity on the pit propagation processes is simply to estimate the evolution of corrosion damage (not only the rate of pit propagation) as a function of time. The potential drop can be regarded as being unimportant if the pit depth, as function of time, can be approximated by a straight line containing the point $x = 0$ at $t = 0$. We report below calculations of this type based on model polarization curves.

We will assume that, in accordance with the laws of electrochemical kinetics, the corrosion current density, i_{corr} , at any given time is determined by the difference between the potential of the metal, E , and the potential in the solution near the electrode surface, ϕ_s , by the concentration of species near the electrode surface, C_{ks} , and by temperature, T , i.e.

$$i_{\text{corr}} = i_{\text{corr}}(E - \phi_s, C_{1s}, C_{2s}, \dots, C_{Ns}, T). \quad (27)$$

Usually, the electrodisolution reaction occurring in the cavity, due to oxidation of the metal, is described in terms of the Tafel equation as

$$i_{\text{corr}} = i_0 \exp \left[\frac{\alpha F (E - U_0 - \phi_s)}{RT} \right] = i^* \exp \left[- \frac{\alpha F \phi_s}{RT} \right]. \quad (28)$$

Here, i_0 is the exchange current density, α is the anodic transfer coefficient, U_0 is the open-circuit potential, and $i^* = i_0 \exp \left[\frac{\alpha F (E - U_0)}{RT} \right]$ is the current density calculated in the absence of a potential drop in the cell. All potentials, E , U_0 , and ϕ_s , are referred to the same reference electrode at infinity. It is convenient to denote

$$i^* = i_0^* f(C_{1s}, C_{2s}, \dots, C_{Ns}), \quad (29)$$

where i_0^* is the corrosion current density under conditions when there are no concentration and potential drops in the solution. We will assume that i_0^* is the initial corrosion current density that is realized in the system after depassivation of the surface. Usually, it is supposed that i_{corr} does not depend on specie concentrations and $f \equiv 1$ [10,16,18]. However, in some cases, a power-law dependence has been assumed [22], i.e.

$$f(C_{1s}, C_{2s}, \dots, C_{Ns}) = \prod_{k=2}^N \left(\frac{C_{k,s}}{C_{k,\infty}} \right)^{\lambda_k}. \quad (30)$$

If ionic species that influence the kinetics of corrosion do not participate in any chemical or electrochemical reactions, their concentrations are described by Eq. (16) and we have for the corrosion current density:

$$i_{\text{corr}} = i_0^* \exp \left[- \frac{\alpha_{\text{eff}} F \phi_s}{RT} \right], \quad (31)$$

where

$$\alpha_{\text{eff}} = \alpha + \sum_{k=2}^N z_k \lambda_k \quad (32)$$

is the effective transfer coefficient. In many practical cases, the corrosion current density depends only on the concentration of Cl^- , in which case Eq. (32) reduces to

$$\alpha_{\text{eff}} = \alpha - \lambda, \quad (33)$$

where λ is the effective kinetic order of the metal dissolution reaction with respect to chloride concentration (for example). Three different cases can occur under these conditions

- (a) $\alpha > \lambda$, i.e. $\alpha_{\text{eff}} > 0$. This is the usual case. Since the value of electric potential at the bottom of the pit increases as the pit propagates, the dissolution rate at the bottom decreases as a function of pit depth (note that ϕ_s is the potential in the solution with respect to a reference electrode at infinity).
- (b) $\alpha = \lambda$, i.e. $\alpha_{\text{eff}} = 0$. In this case, the accelerating action of anions on the electrode reaction completely compensates for the increasing potential drop in the solution during pit growth. The dissolution rate does not change with pit length or time and equals its initial value.
- (c) $\alpha < \lambda$, i.e. $\alpha_{\text{eff}} < 0$. In this last case, the accelerating action of anions on the electrode reaction outweighs the inhibiting effect that arises from the increase in the potential drop in the cavity environment, as the pit grows. Acceleration of the pit growth rate with time has been noted in the literature [34].

Assuming that the shape of the cavity does not change with time (for example, an initially hemispherical pit retaining this form), we can reduce the problem of calculating the cavity depth to the solution of the ordinary differential equation

$$\frac{dx}{dt} = V_s(x) = K_V i_{\text{corr}}. \quad (34)$$

We have solved this equation using the simple Euler method, which is, however, sufficiently accurate for the problem at hand, i.e. we calculated

$$x(t + \Delta t) = x(t) + V_s(x)\Delta t. \quad (35)$$

The function $V_s(x)$ is calculated in the following way. First of all, for a given value of the pit depth, x , we calculate the quasipotential of the system at the electrode surface, q , using Eq. (9). The current density, i_{corr} , is then calculated from Eq. (27) using values of the concentration and potential from the previous step. Using this value of q , we then calculate new values for the potential and surface concentrations by the numerical solution of Eq. (23) [or Approximation (25)], followed by substitution of ϕ into Eqs. (16) and (17). Then we recalculate a new value of i_{corr} using Eq. (27) and perform the next step in the calculation. The initial conditions are obvious: $x = 0$, $\phi_s = 0$, and $C_k = C_{k\infty}$ ($k = 1, 2, \dots, N$) at $t = 0$.

For estimation purposes, we suggest a very simple analytical equation for calculating pit depth as a function of time, when the corrosion current density obeys Eq. (31). The equation for calculating the current density on the electrode surface as a function of pit depth can be obtained by substituting Eq. (25) into Eq. (31), which yields

$$i_{\text{corr}} = i_0^* \left[\frac{\sqrt{\delta_1^2(n+1)^2 + 4\delta_2(n+2)[\delta_2(n+2) + \delta_1(n+1) + q/q_0]} - \delta_1(n+1)}{2\delta_2(n+2)} \right]^{-\alpha_{\text{eff}}} \quad (36)$$

If we expand the expression in brackets into a Taylor series in the quasipotential, q , and restrict ourselves to the linear term, we obtain the simple expression;

$$i_{\text{corr}} = i_0^* [1 + Bi_{\text{corr}}x]^{-\alpha_{\text{eff}}}, \quad (37)$$

where we have substituted $q = ai_{\text{corr}}x$ [see Eq. (9)] and have denoted

$$B = \frac{a}{q_0[\delta_1(n+1) + 2\delta_2(n+2)]}. \quad (38)$$

Eq. (37) has no analytical solution for an arbitrary value of α_{eff} , but it is easy to solve for small and large values of the parameter B . For $B \ll 1$, the expression in brackets in Eq. (37) approximately equals 1, and we simply have $i = i_0^*$. On the other hand, for $B \gg 1$ we have $i = i_0^* / [Bi_0^*x]^{\alpha_{\text{eff}}/(1+\alpha_{\text{eff}})}$.

The form of these limits suggests a simple interpolation formula, as follows:

$$i_{\text{corr}} = \frac{i_0^*}{(1 + Bi_0^*x)^{\alpha_{\text{eff}}/(1+\alpha_{\text{eff}})}}, \quad (39)$$

which can be used for any arbitrary value of the parameter B .

From Eq. (39) and Faraday's law, we then obtain the following simple expression for pit depth as a function of time:

$$x = x_0[(1 + t/t_0)^m - 1], \quad (40)$$

where the power, m , has the form

$$m = \frac{\alpha_{\text{eff}} + 1}{2\alpha_{\text{eff}} + 1} \quad (41)$$

and

$$x_0 = 1/(Bi_0^*), \quad t_0 = mx_0/v_0 \quad \text{and} \quad v_0 = i_0^*/K_V. \quad (42)$$

It is evident that v_0 is simply the initial pit propagation rate. For small times ($t \ll t_0$), when the potential drop has an insignificant influence on the current density, as follows from Eq. (40), the pit depth, x , can be represented as a linear function of t

$$x = v_0t \quad (43)$$

and for large times ($t \gg t_0$), x takes the power form

$$x = x_0(t/t_0)^m = kt^m, \quad (44)$$

where $k = x_0/t_0^m$.

The velocity of pit propagation is obtained by differentiating Eq. (40) to yield

$$v = \frac{dx}{dt} = v_0 \left(1 + \frac{t}{t_0}\right)^p, \quad (45)$$

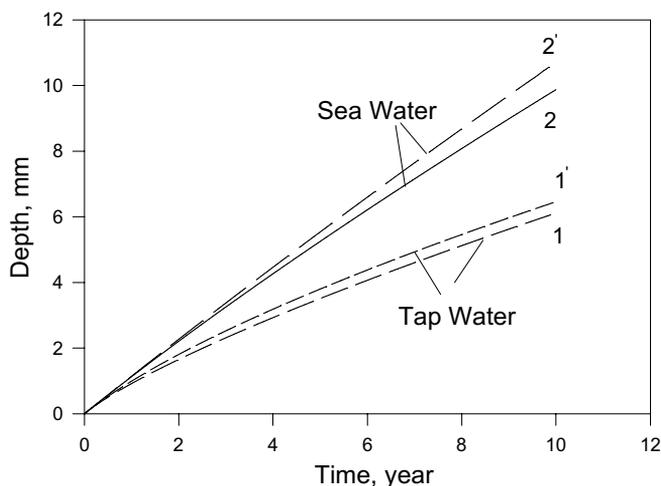


Fig. 7. The depth of a hemispherical pit as a function of time for tap water ($[\text{NaCl}] = 0.007 \text{ M}$ and $[\text{Na}_2\text{SO}_4] = 0.054 \text{ M}$) and sea water ($[\text{NaCl}] = 0.5 \text{ M}$) at $T = 25 \text{ }^\circ\text{C}$, $\alpha_{\text{eff}} = 1$ and $i_0^* = 10^{-4} \text{ A/cm}^2$. Curves 1 and 2 are calculated numerically and 1' and 2' by using Eq. (40).

where

$$p = m - 1 = -\frac{\alpha_{\text{eff}}}{2\alpha_{\text{eff}} + 1}. \quad (46)$$

Fig. 7 illustrates the accuracy of proposed approximate solution [Eq. (40)].

So far in our calculations, some assumptions that are not always fulfilled under real conditions have been made. Thus, we assumed that a pure metal, but not an alloy, is corroded, that there are no homogeneous chemical reactions in the electrolyte, and that the electrolyte is stagnant. We discuss these assumptions below.

4.1. Corrosion of alloys

A comprehensive treatment of this issue will be published at a later date, so that only some of the principal results are briefly discussed here. Let us suppose that the alloy consists of M metal components and that index $m = 1, 2, \dots, M$ denotes each of these components. We also denote the mass fraction of each component by $x_m = \rho_m / \rho$, where ρ_m is the partial density of the component m in the alloy and $\rho = \sum_{m=1}^M \rho_m$ is the density of the alloy. For simplicity, in the first step, we suggest that dissolution of each component of the alloy, Me_m , can be described by a simple reaction



and that the dissolution of the alloy is uniform. The term “uniform dissolution” means that all for the normal surface fluxes of the metals the following condition holds:

$$J_{sm} = P_m J_{s1}, \quad m = 2, 3, \dots, M, \quad (48)$$

where

$$P_m = \frac{x_m \mu_1}{x_1 \mu_m}. \quad (49)$$

Here, the component with $m = 1$ is chosen as the reference component. It can be shown that for species with $m = 2, 3, \dots, M$, the relation

$$\vec{J}_k = P_k \vec{J}_1, \quad k = 2, 3, \dots, M, \quad (50)$$

holds not only on the electrode surface but everywhere in the electrolyte. Using this condition, it can be shown that the expression for the current density can be written in the form of Ohm's law [see Eq. (18)] with the effective conductivity, κ_{eff} , being defined by the expression

$$\kappa_{\text{eff}} = F z_1 D_1 C_1 + F D_1 \left(G_1 + \frac{z_1 F C_1}{RT} \right) \left(z_1 + \sum_{k=2}^M z_k P_k \right), \quad (51)$$

where

$$G_1 \equiv \frac{dC_1}{d\phi} = \frac{F}{RT} \frac{\sum_2^N z_k^2 C_k - z_1 C_1 \sum_2^M z_k P_k D_1 / D_k}{z_1 + \sum_2^M z_k P_k D_1 / D_k}. \quad (52)$$

The concentrations of non-active species [i.e. those not involved in Reactions (47)] in the solution ($k = M, M + 1, \dots, N$) as a function of potential, can be found from Boltzmann's distribution law [see Eq. (16)]. On the other hand, the concentrations of the electroactive species ($k = 1, 2, \dots, M$) as a function of potential, can be found from the electroneutrality condition and the following system of ordinary differential equations:

$$D_k \left(\frac{dC_k}{d\phi} + \frac{z_k F}{RT} C_k \right) = P_k D_1 \left(\frac{dC_1}{d\phi} + \frac{z_1 F}{RT} C_1 \right), \quad k = 2, 3, \dots, M, \quad (53)$$

with boundary conditions $C_k = C_{k\infty}$ at $\phi = 0$.

Subsequent treatment of this case practically coincides with the approach that is described above for a pure metal. The only change that must be introduced for describing alloy corrosion in comparison with pure metals is that instead of Eq. (19) for the effective conductivity we must use Eq. (52). For the case of the pure metal ($M = 1$) both equations coincide.

The difference in pit propagation rate in alloys, compared with that in pure metals, depends on two factors. Firstly, it depends on the differences in the polarization characteristics, which are often dictated by alloy components, and secondly, it depends on differences in the mass transport conditions. To investigate the influence of the second factor, we compared pit propagation rates for pure iron and a hypothetical alloy that has the same density and polarization behavior as pure iron, but has the following mass fraction composition: Fe—71%, Ni—12%, and Cr—17%. This composition is typical of stainless steels. It is assumed that the effective valence, n , equals 2 for Fe and Ni and 3 for Cr.

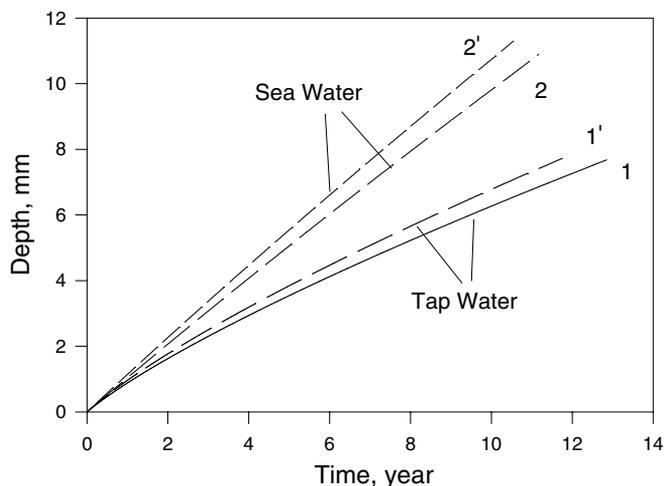


Fig. 8. The depth of a hemispherical pit as a function of time for tap water ($[\text{NaCl}] = 0.007 \text{ M}$ and $[\text{Na}_2\text{SO}_4] = 0.054 \text{ M}$) and sea water ($[\text{NaCl}] = 0.5 \text{ M}$) at $T = 25 \text{ }^\circ\text{C}$, $\alpha_{\text{eff}} = 1$, and $i_0^* = 10^{-4} \text{ A/cm}^2$. Curves 1 and 2 are calculated for pure iron and 1' and 2' for hypothetical alloy.

Numerical calculations of the potential distribution in the pit as a function of time show no significant difference between the alloy and pure iron. However, there is a visible discrepancy in the depth of a hemispherical pit as a function of time [see Fig. 8]. This discrepancy can arise only from the difference in the electrochemical equivalent volume, K_V , which for the case for the alloy can be calculated from the equation

$$K_V = \frac{1}{\rho F \sum_{m=1}^M x_m n_m / \mu_m}. \quad (54)$$

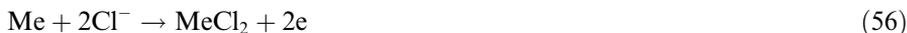
We see that the mass transfer conditions in the solution practically do not change for the given values of the parameters. This conclusion can also be predicted from sensitive analysis (see Figs. 4 and 5).

4.2. Homogeneous chemical reactions

The complexation reactions of metals (especially for Ni and Cr) in corrosion systems are well known. To investigate the influence of these reactions on the mass transfer conditions, we consider the limiting case when the influence of the homogeneous chemical reactions is maximal. This case occurs when all dissolving metal ions immediately participate in homogeneous chemical complexation reaction with Cl^- resulting in the formation of MeCl^+ and MeCl_2 complexes (for the case of $n = 2$). This situation is equivalent to the assumption that there are two electrochemical reactions on the electrode surface



and



We will investigate the influence of the complexation assuming that metal Me corrodes in NaCl in accordance with only one of the Reactions (55) and (56). If this influence will be unimportant for some region of concentration it would be naturally to assume that this influence will be unimportant when these reactions take place simultaneously. Solution of the system of mass transport equations (13)–(15) yields:

$$\phi = \frac{RT}{F} \frac{D_1 + D_2}{D_1 - D_2} \text{Ln} \left[1 - \frac{q(1 - D_2/D_3)}{4FD_2C_\infty} \right] \quad (57)$$

for the case of Reaction (55) and

$$\phi = -\frac{RT}{F} \text{Ln} \left[1 - \frac{q}{2FD_1C_\infty} \right] \quad (58)$$

for the case of Reaction (56). Here C_∞ is the bulk concentration of NaCl, D_1 , and D_2 are the diffusion coefficient for Cl^- and MeCl^+ , correspondingly.

Comparison of Figs. 9 and 6 shows that for $[\text{NaCl}] \geq 0.5 \text{ M}$ there is no significant influence of complexation on the potential distribution and, accordingly, on the kinetics of pit growth for the practical region of $q \leq 10^{-4} \text{ A/cm}$. It is interesting to note the sharp increase of potential if only Reaction (58) takes place. As follows from Eq. (58), $\phi \rightarrow \infty$ at $q \rightarrow 2FD_1C_\infty$. In this case, the concentrations of all species (and conductivity of electrolyte) near the electrode surface go to 0 and corrosion for $q > 2FD_1C_\infty$ can take place only under diffusion control resulting from the transport

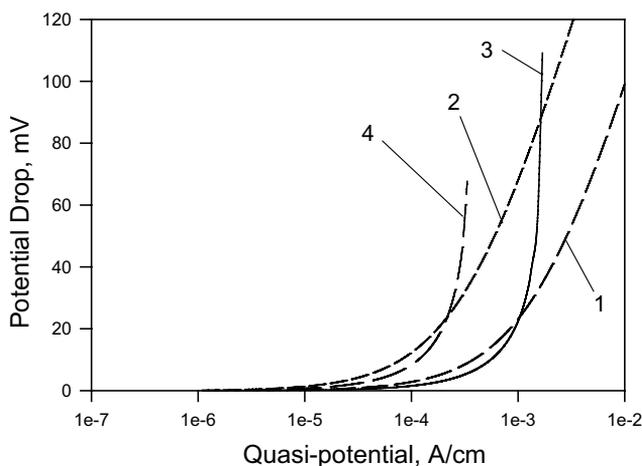


Fig. 9. The potential drop as a function of quasipotential for dissolution of a hypothetical metal ($n=2$) as a result of electrochemical Reaction (55) (Curves 1 and 2) or Reaction (56) (Curves 3 and 4) in 0.5 M NaCl (Curves 1 and 3) or 0.1 M (Curves 2 and 4) at $T = 25^\circ \text{C}$. The ratio $D_1/D_2 = 2.87$ is taken from Ref. [18] for Cl^- and NiCl^+ ions.

of Cl^- to the electrode surface. For the case of Reaction (57), such limitations can take place only for $D_2/D_3 < 1$.

Of course, in the general case, other complexes (e.g. MeCl_3^-) may exist in the solution. However, it seems unlikely, at least for normal temperatures and not very high concentrations, that these complexes can significantly influence the corrosion process.

4.3. Influence of convection

At sufficiently high flow rates, fluid flow in the bulk environment is known to reduce the rate of localized corrosion [17]. This phenomenon is related to rinsing out of the corrosion cavity, which leads to an increase in the resistance to charge transfer inside the pit and in turn to a decrease in the potential drop. However, if the cavity is sufficiently deep and of a high aspect ratio (not the case here), increasing flow rate may actually increase the rate of cavity growth by enhancing the mass transport of oxygen to the external surface. Let us consider the limiting case of intensive convection, when no concentration gradients exist within the pit. Under these conditions, Ohm's law is obeyed and solution of the transport problem reduces to solving the following equation:

$$i_{\text{corr}} = i_0^* \exp \left[-\frac{\alpha F \phi_s}{RT} \right] = \frac{\kappa \phi_s}{ax}. \quad (59)$$

It can be shown by numerical analysis that solution of this equation can be approximated by

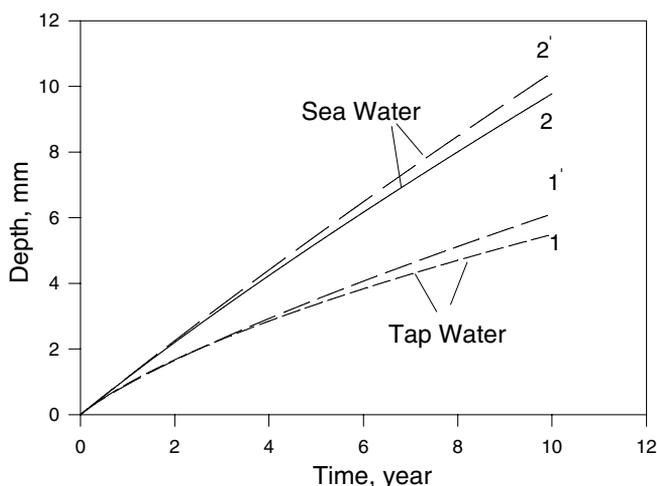


Fig. 10. The depth of a hemispherical pit as a function of time for tap water ($[\text{NaCl}] = 0.007 \text{ M}$ and $[\text{Na}_2\text{SO}_4] = 0.054 \text{ M}$) and sea water ($[\text{NaCl}] = 0.5 \text{ M}$) at $T = 25 \text{ }^\circ\text{C}$, $\alpha_{\text{eff}} = 1$ and $i_0^* = 10^{-4} \text{ A/cm}^2$. Curves 1 and 2 are calculated in the presence of intensive convection and 1' and 2' without convection.

$$\exp \left[-\frac{\alpha F \varphi_s}{RT} \right] = \frac{1}{(1 + 1.2gx)^{0.7}}, \quad (60)$$

with an accuracy of not less than 4% for $0 \leq gx \leq 100$, where

$$g = \frac{ai_0^* \alpha F}{\kappa RT}. \quad (61)$$

After application of Faraday's law, it is easy to show that the pit depth as a function of time can be described by Eq. (40) with

$$m = 0.588, \quad L_0 = 1/(1.2g) \quad \text{and} \quad t_0 = 1/(2.04gi_0^*K_V). \quad (62)$$

Fig. 10 shows that the influence of convection is not very great, at least for $i_0^* \leq 10^{-4}$ A/cm².

5. Discussion

The theory developed above allows us to estimate the importance of the electrolyte resistance on the rate of corrosion cavity (e.g., pit) propagation. This can be easily done if the polarization curve [corrosion current density vs. potential, see Eq. (27)] is known. Thus, experimental data for the dissolution of Type 316 L stainless steel in chloride solutions can be approximated by the following expression:

$$i_{\text{corr}} = 0.9 \times 10^{-6} C^{1.27} \exp \left[\frac{0.6FE}{RT} \right] \quad (63)$$

for $0.01 \text{ M} \leq C \leq 4 \text{ M}$, and $0.2 \text{ V} \leq E \leq 0.3 \text{ V}$ at $T = 23 \text{ }^\circ\text{C}$ [35]. Here C is the molar concentration of NaCl and E is the potential of the metal vs. SHE. The corrosion potential for this system, calculated by using standard OLI commercial software [35–37], yields $E_{\text{corr}} \approx 0.236 \text{ V}$ (SHE) for a concentration of oxygen of $0.25 \times 10^{-3} \text{ M}$ (concentration of O₂ under normal aeration conditions). This means that, under the given conditions, i_{corr} can be presented in the form of Eqs. (28) or (31) by letting $E = E_{\text{corr}}$. Figs. 11 and 12 show that some deviation from the linear propagation law is observed only for the highest concentration of NaCl (4 M). More precisely, an acceleration of pit propagation is observed. Acceleration occurs because, under the given conditions, the accelerating action of anions on the electrode reaction outweighs the inhibiting effect that arises from the increase in the potential drop in the crevice environment, as the pit grows ($\alpha_{\text{eff}} = \alpha - \lambda = 0.6 - 1.27 = -0.67 < 0$). However, this acceleration is predicted to be observed only in the non-practical region, when the depth of the pit exceeds 2 cm. Accordingly, under real conditions, we conclude that there is no significant potential drop in corrosion cavities on Type 316 L stainless steel and open pits must propagate in this steel at a constant rate.

For the case when the polarization curve is not known, it is possible to estimate the significance of the potential drop in a hemispherical pit. Let us assume, for example, that an experiment shows that a pit has the depth, x , at observation time, t , yielding the following average corrosion rate $i_{\text{av}} = (x/t)/K_V$. The average current

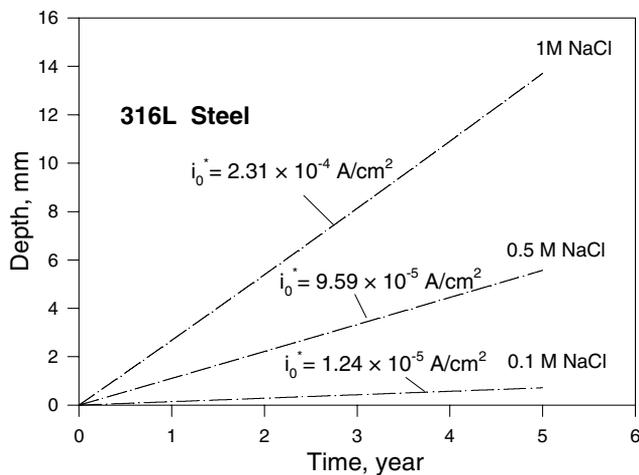


Fig. 11. Predicted depth of a hemispherical pit as a function of time for corrosion of 316 L stainless steel in NaCl solution at $T = 23\text{ }^\circ\text{C}$.

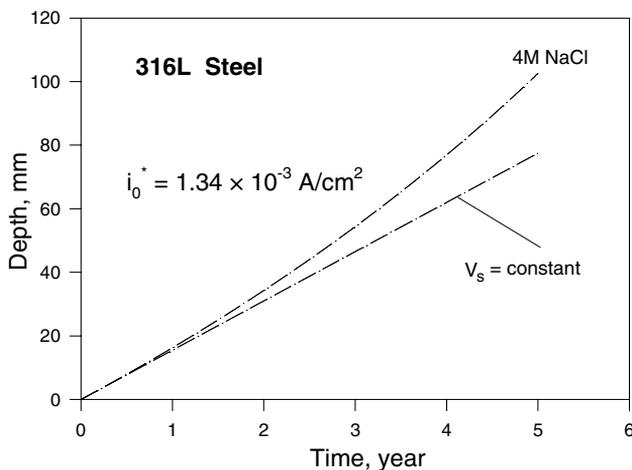


Fig. 12. Predicted depth of a hemispherical pit as a function of time for corrosion of 316 L stainless steel in high concentrated 4 M NaCl solution at $T = 23\text{ }^\circ\text{C}$. For comparison, pit propagation at a constant rate, V_s , is shown.

density can be also estimated by using the anticipated values of x_{cr} and t_s as $i_{av} = (x_{cr}/t_{cr})/K_V$. Substituting the value of the quasipotential $q = ai_{av}x_{cr} = a(x_{cr}^2/t_{cr})/K_V$ into Eq. (25) [or into Eq. (26) in the simplified case] yields the upper estimate for the potential drop, ϕ_s , in a hemispherical pit in a stagnant electrolyte. In the case of a hemispherical pit in a well-mixed electrolyte, we simply have from Eq. (59) the following expression for the potential drop

$$\phi_s = \frac{ai_{av}x_{cr}}{\kappa} = \frac{ax_{cr}^2}{\kappa t_s K_V}. \quad (64)$$

If the value, ϕ_s , is small (let say within 5–10 mV), then we conclude that there is no significant potential drop in this case and that the pit will propagate at a constant rate under constant external conditions.

As an example, let us consider the case of metal or alloy ($n = 2$) corrosion in 0.5 M NaCl solution (seawater). Let us suppose, also, that we know from the experiment that the depth of the largest pit does not exceed 1 mm after one year of corrosive attack. Assuming that the corrosion process takes place at a uniform rate, we can estimate from Faraday's law that the average corrosion current density, i_{av} , does not exceed 10^{-4} A/cm² (0.86×10^{-4} A/cm² in the case of Fe corrosion) and, accordingly, that the quasipotential, $q = ai_{av}x$, does not exceed 10^{-4} A/cm. Eq. (26) [see also Fig. 6] shows that the corresponding potential drop, ϕ_s , does not exceed 1 mV for a hemispherical, open pit. It is clear that such a small potential drop is insignificant and the assumption of a constant pit propagation rate under constant external conditions is justified. Using Eq. (26), we can predict also that the growth of the pit will take place at a constant rate up to about 1 cm in depth (after 10 years of service). Under these conditions, the corresponding potential drop, ϕ_s , does not increase above 3.5 mV. For the case of intensive convection, Eq. (64) yields the following upper estimate for the value of the potential drop; $\phi_s = 5.6$ mV for 10 years of service life.

We can summarize this example as follows. If the depth of an open pit does not exceed 1 mm after one year, the critical size of the system is of the order of 1 cm, and the concentration of [NaCl] is comparable to that of sea water (or exceeds this value), the resistance of the electrolyte phase does not influence the rate of corrosion (uniform rate). Or, in other words, under normal conditions, in sufficiently concentrated electrolytes (with the order or more than seawater), the pit propagation rate must be constant.

Analogously, we can predict that for pitting corrosion in tap water, when the maximum depth of the pit is of the order of 1 mm and the service life of the system is not less than 10 years, there is no significant potential drop in the solution and hence the pit propagation rate is again constant.

It is important to note that the maximum value of the quasipotential is proportional to x_{cr}^2/t_s , i.e. it sharply decreases with decreasing critical dimension of the system [see Eq. (12)]. Analysis shows that for a system having $x_{cr} = 0.1$ mm and a service life of not less than 1 year, pit propagation can be regarded as being constant, even when the bulk concentration of NaCl is as low as 5×10^{-4} M. On the other hand, for a system with a very large service life ($t_s \geq 100$ years), the average corrosion current density must be so low that the pit propagation rate is constant for invariant external conditions (for x_{cr} of order of 1 cm and [NaCl] $\geq 5 \times 10^{-2}$ M). It is also important to note that, in the case of pit propagation at a constant rate, the average current density, i_{av} , equals the initial current density, i_0^* .

Generally speaking, the value of the potential drop in a corrosion cavity of depth, x , depends on the ratio q/q_0 [see Eq. (25)], which is proportional to the ratio $i_0^*/C_{t,an}$.

If the initial current density, i_0^* , does not depend on the concentration of any species, and if the value of bulk concentration, $C_{t,an}$ is sufficiently low, significant potential drops exist inside and outside the corrosion cavity and hence the cavity growth cannot occur at a constant rate. Stress corrosion cracking in boiling water reactors, where $C_{t,an}$ is of the order of 10^{-6} – 10^{-5} M, is an example of such a system [19]. However, in a system where the initial dissolution current density, i_0^* , depends on the concentration, $C_{t,an}$, the ratio $i_0^*/C_{t,an}$ remains approximately constant or even decreases with decreasing $C_{t,an}$. In these systems, cavity propagation at a constant rate is predicted also for a very low bulk concentration of the electrolyte. The corrosion of 316 L stainless steel is an example of such a system (see Fig. 11, where the values of the initial corrosion current densities are indicated).

In some systems, the pit propagation rate may be constant, in spite of a significant potential drop in the cavity. This occurs when the absolute value of parameter p in Eq. (45) is low ($|\alpha_{eff}|$ is low), i.e. when the accelerating action of anions on the electrode reaction compensates for the increasing potential drop in the solution during pit growth.

It is important to note that the initial current density, i_0^* , under normal conditions cannot exceed the order of 10^{-4} A/cm². Only in some extreme cases, such as corrosion in highly concentrated, aggressive solutions, where the rate of corrosion is of the order of 1 cm/year, is i_0^* of the order of 10^{-3} A/cm². Fig. 13 shows that, for such a high value of i_0^* , the pit propagation rate is observed to deviate from the linear law. However, even under these conditions, in highly concentrated electrolytes (and only in concentrated electrolytes is such a high corrosion rate observed), the corrosion rate can be regarded as being constant within the first year of observation. The

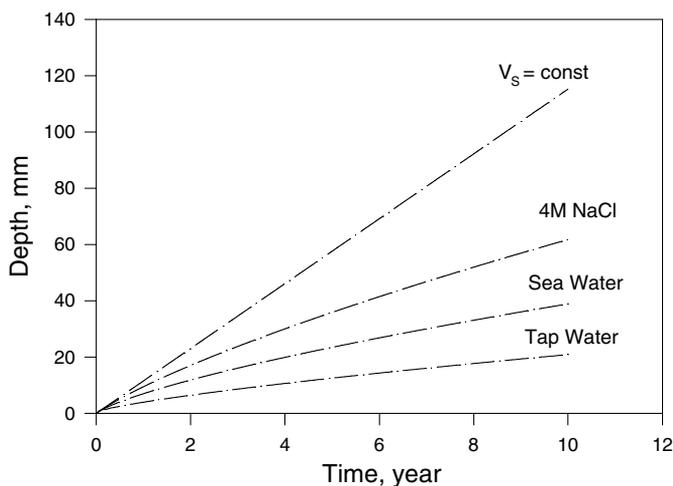


Fig. 13. Predicted depth of a hemispherical pit as a function of time for iron in NaCl solution at $T = 25$ °C, $\alpha_{eff} = 1$ and $i_0^* = 10^{-3}$ A/cm². For comparison, pit propagation at a constant rate, V_s , is shown.

predicted damage for $t > 1$ year becomes increasingly unrealistic if the pit propagation rate is assumed to be constant and equal to the initial rate.

We see that, if the initial current density is more than 10^{-3} A/cm², the service life must be shorter than one year for a critical dimension of 1 cm. However, much higher values of i_0^* , such as 10^{-3} – 1 A/cm², or even 1 – 10^6 A/cm², are described (measured or employed) in the literature [22], implying an uncharacteristically short service life. How can that be?

Several explanations of this position are evident. Firstly, the experiments may have been performed under highly non-steady-state conditions or even under galvanostatic or potentiostatic conditions. In the latter case, the potentiostat essentially presents a zero output impedance and whatever current is necessary to satisfy the control function is supplied by the instrument. This is clearly not in consonance with freely corroding conditions, where the (coupling) current exiting the cavity must be consumed on the adjacent external surface by an appropriate cathodic reaction that is subject to a significant impedance at the interface in addition to the solution resistance. In the case of galvanostatic control, the galvanostat supplies whatever output voltage is necessary to supply the preselected current. Measurement of the coupling current for stress corrosion cracking in Type 304 SS in high [38] and ambient [39] temperature solutions under open circuit conditions shows it to be of the order of a few microamps to a few tens of microamps, and a similar current, suitably scaled for the difference in cavity area, is expected for pitting. Accordingly, the coupling current for the growth of an individual pit under free corrosion conditions is almost certainly at the nano amp to tens of nano amp level and is far below what is normally imposed under potentiostatic conditions in the laboratory. Recognition of the importance of coupling between the internal and external environments is the basis of the various “coupled environment” models for SCC, pitting, and corrosion fatigue that have been developed by the authors [19,24].

The second explanation is that modeling calculations were made for metal potential values, E , that are significantly higher than the free corrosion potential, E_{corr} , under real conditions. The third explanation is as follows. It has been tacitly assumed that the polarization curve always exists in the form of Eq. (27). However, it may not always be so. In the general case, the polarization curve may depend also on time, t , i.e.

$$i_{\text{corr}} = i_{\text{corr}}(E - \varphi_s, C_{1s}, C_{2s}, \dots, C_{Ns}, T, t). \quad (65)$$

In other words, the polarization curve may differ significantly during the initial and the main stages of pit propagation. For example, Fig. 14 shows pit propagation in an aluminum alloy in tap water [40]. We see that the propagation curve can be approximated by the usual power law: $x = kt^m$. We also see that these data can be approximated by a linear function. However, this linear function does not extrapolate to the point, $x = 0$ at $t = 0$. Thus, we can imagine the following situation. During the initial stage of pit propagation (during the initial period of time, t_{in}), the passive film on the active surface is totally destroyed, the current density is very high, and the pit attains a depth of x_{in} . During this initial stage, significant potential and concentration drops exist within the pit. For the case shown in Fig. 14, the duration

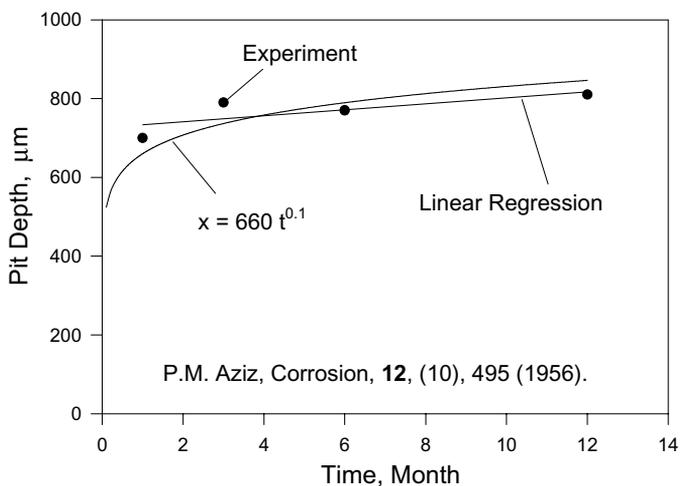


Fig. 14. Pitting rate curve for Alcan 2S-O in Kingston tap water.

of this period appears to be less than 1 month. Subsequently, a partially protective (e.g., “salt”) film forms on the active surface. This film can arise, for example, from the precipitation of products of the electrochemical dissolution reaction. The corrosion current density then sharply decreases and the corresponding potential and concentration drops also sharply decrease. Further growth of the pit takes place at a relatively constant propagation rate. The theory developed above can be used to describe this latter stage. However, we must note that if the pit has an initial depth, x_{in} , at an initial time, t_{in} , Eq. (40) must be rewritten in the form

$$x = x_{in} + x_0[(1 + (t - t_{in})/t_0)^m - 1], \quad (66)$$

where the parameters, x_0 , t_0 , and m have the same meanings as previously defined. Of course, if $x_{in} \ll x_{cr}$ no changes in the theory are required.

We would like to emphasize that the theory developed in this work has an absolutely formal character. Thus, nowhere in this work have we attempted to explain the mechanism of stabilization of propagating pits in the “constant rate” regime. Starting from the observed values of service life, we only show that in real, open cavities (under transport conditions that are not significantly more severe than the transport conditions that exist in an hemispherical pit) the potential drop, ϕ_s and the concentration drops of dissolving metal ions, ΔC , are subject of some limitations that follow from Faraday’s law. Thus, ΔC cannot be greater than 0.1–0.01 M and ϕ_s cannot be larger than ca. 10 mV for the corrosion of steels in seawater. However, as has been noted in numerous articles much larger potential and concentration drops must be present in cavities to ensure the stability of pit growth. Under these circumstances, the question arises about the driving force for localized corrosion.

A possible resolution of this discrepancy is that even small values of the potential and concentration drops can result in stabilization of pit propagation rate under real conditions. The second explanation is that, in real systems, the transport conditions are significantly more severe than the transport conditions that exist in a hemispherical pit. The third explanation is connected with the possible discontinuous character of pit propagation. It may be that an active stage of pit propagation (when high potential and concentration drops, and hence high corrosion current density, exist within the cavity) give way to a passive stage where $i_{\text{corr}} \approx 0$ and therefore the potential and concentration drops disappear. These two stages might alternate, thereby sharply reducing the observed average value of the pit propagation rate. Pit propagation under such “pulsating” conditions has been observed experimentally [22].

Of course, our estimation of the small influence of ϕ_s on the rate of pit propagation, in real systems is based on the assumption that the dependence of i_{corr} on ϕ_s is not stronger than that given by Tafel's equation with the anodic transfer coefficient, α , being of the order of 1. We regard this assumption to be reasonable.

Finally, the theory developed in this work does not imply that it is possible to predict long-term corrosion damage by a simple, linear extrapolation of the pit depth. This is, because localized corrosion in general, and pitting corrosion in particular, is a progressive phenomenon, in which new damage nucleates as existing pits grow and die (passivate). The present theory does, however, provide guidance on the kinetics of growth of individual pits within this progressive evolution scenario, but the extrapolation of damage must be made upon the basis of Damage Function Analysis [41] or Extreme Value Statistics [42], as will be discussed in a forthcoming article.

6. Summary and conclusions

It has been shown that, for localized corrosion (e.g., pitting corrosion) under real, practical conditions, typical values of the critical dimension of the system and the service life impose restrictions on the corrosion current densities (averaged and initial) that must exist within the corrosion cavity. Thus, we show that the initial current densities in real, open pits cannot exceed values of 10^{-4} – 10^{-3} A/cm², with the understanding that the polarization curve (corrosion current density vs. potential) does not change as the pit evolves. Simple analytical expressions for predicting potential and concentration drops in corrosion cavities, and for calculating cavity propagation rate, in a system containing uni- and bi-valent anions have been obtained. These expressions can be used to extrapolate the results of short-term corrosion experiment to future times within the framework of Damage Function Analysis or Extreme Value Statistics. In particular, it is shown that if localized corrosion takes place in an electrolyte having a conductivity that is of the order of that of seawater, it is possible to neglect the potential drop in the corrosion cavity and to consider the rate of pit propagation as being constant. The same conclusion holds for the pitting of 316 L steel, for practically any concentration of electrolyte.

Acknowledgements

The authors gratefully acknowledge the support of this work by the National Institute of Standards through the Advanced Technology Program (co-sponsored by ChevronTexaco, DuPont, Exxon Mobil, Mitsubishi Chemical Co, and Shell Oil Co.) and by the Electric Power Research Institute.

References

- [1] S.M. Sharland, *Corros. Sci.* 27 (1987) 289.
- [2] A. Turnbull, *Br. Corros. J.* 28 (1993) 297.
- [3] H.S. Isaacs, *J. Electrochem. Soc.* 120 (1973) 1456.
- [4] J.V. Tester, H.S. Isaacs, *J. Electrochem. Soc.* 122 (1975) 1438.
- [5] R. Alkire, D. Ernsberger, D. Damon, *J. Electrochem. Soc.* 123 (1976) 456.
- [6] H.W. Pickering, R.P. Frankenthal, *J. Electrochem. Soc.* 119 (1972) 1297.
- [7] D.G. Ateya, H.W. Pickering, *J. Appl. Electrochem.* 11 (1981) 453.
- [8] J.R. Galvele, *J. Electrochem. Soc.* 123 (1976) 464.
- [9] S.M. Gravano, J.R. Galvele, *Corros. Sci.* 24 (1984) 517.
- [10] S.M. Sharland, P.W. Tasker, *Corros. Sci.* 28 (1988) 603.
- [11] S.M. Sharland, C.P. Jackson, A.J. Diver, *Corros. Sci.* 29 (1989) 1149.
- [12] J.C. Walton, *Corros. Sci.* 30 (1990) 915.
- [13] J.C. Walton, G. Grangolino, S.K. Kalandros, *Corros. Sci.* 38 (1996) 1.
- [14] J. Newman, D.N. Hanson, K. Vetter, *Electrochim. Acta* 22 (1977) 829.
- [15] M.V. Verbrugge, D.R. Bakker, J. Newman, *Electrochim. Acta* 38 (1993) 1649.
- [16] J.N. Harb, R.C. Alkire, *J. Electrochem. Soc.* 138 (1991) 2594.
- [17] J.N. Harb, R.C. Alkire, *J. Electrochem. Soc.* 138 (1991) 2568.
- [18] M.V. Verbrugge, D.R. Bakker, J. Newman, *J. Electrochem. Soc.* 140 (1993) 2530.
- [19] D.D. Macdonald, M. Urquidi-Macdonald, *Corros. Sci.* 32 (1991) 51.
- [20] D.D. Macdonald, C. Liu, M. Urquidi-Macdonald, et al., *Corrosion* 50 (1994) 761.
- [21] Z. Szklarska-Smialowska, *Pitting Corrosion of Metals*, National Association of Corrosion Engineers, Houston, 1986.
- [22] L.I. Freiman, *Progress in Science and Technology*, in: *Corrosion and Corrosion Protection*, vol. 11, VINITI, 1985, p. 3 (in Russian).
- [23] Y.A. Popov, S.N. Sidorenko, *Theory of Interaction of Metals and Alloys with a Corrosion Environment*, Cambridge Int. Sci. Publ., Cambridge, 1998.
- [24] G. Engelhardt, M. Urquidi-Macdonald, D.D. Macdonald, *Corros. Sci.* 39 (1997) 419.
- [25] J.L. Luo, M.B. Ives, *J. Electrochem. Soc.* 144 (1997) 3907.
- [26] N.J. Laycock, S.P. White, *J. Electrochem. Soc.* B8 (2001) 264.
- [27] Y. Wang, H.W. Pickering, *J. Electrochem. Soc.* 142 (1995) 2986.
- [28] S. Lau, Y.A. Chang, *Scr. Metall.* 8 (1973) 745.
- [29] P.C. Pistorius, G.T. Burstein, *Philos. Trans. R. Soc. Lond.* 341 (1992) 531.
- [30] B. Pilay, J. Newman, *J. Electrochem. Soc.* 140 (1993) 414.
- [31] J. Newman, D.N. Hanson, K. Vetter, *Electrochim. Acta* 23 (1977) 829.
- [32] J. Newman, *Electrochemical Systems*, Prentice-Hall, Englewood Cliffs, NJ, 1992.
- [33] A. Anderko, M. Lencka, *Ind. Chem. Res.* 37 (1998) 2878.
- [34] D.D. Macdonald, C. Liu, M. Urquidi-Macdonald, G. Stickford, B. Hindin, A.K. Agrawal, *Corrosion* 50 (1985) 761.
- [35] A. Anderko, N. Sridhar, D.S. Dunn, *Corros. Sci.*, in press.
- [36] A. Anderko, R.D. Young, *Corrosion* 57 (2000) 543.
- [37] A. Anderko, P.M. McKenzie, R.D. Young, *Corrosion* 58 (2001) 202.

- [38] P.M. Manahan Sr., D.D. Macdonald, A.J. Peterson Jr., *Corros. Sci.* 37 (1) (1995) 189–208.
- [39] M. Gomez-Duran, D.D. Macdonald, *Corros. Sci.* 45 (2003) 1455.
- [40] P.M. Aziz, *Corrosion* 12 (10) (1956) 495.
- [41] G. Engelhardt, D.D. Macdonald, *Corrosion* 54 (1998) 469.
- [42] T. Shibata, *Corros. Eng.* 37 (1988) 699.