On the extension of CP models to address cathodic protection under a delaminated coating

Kerry N. Allahar, Mark E. Orazem *

Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, USA

ABSTRACT

Cathodic protection models for pipeline and other metallic structures developed to address the presence of coating flaws or holidays do not account explicitly for the presence of a delaminated region surrounding a holiday. The potential drop in the delaminated region was obtained by solving the coupled, non-linear, partial differential, governing equations that describe transport and electrochemical reactions within the delaminated region. The results were used to develop an analytic expression for the potential drop across the delaminated region as a function of delaminated region length and the resistivity of the bulk environment exterior to the holiday. Expressions developed using this approach can be utilized by existing cathodic protection models to deliver improved potential distributions along protected metallic surfaces. The simulations were used to test the commonly employed assumption that transport by diffusion can be neglected in the delaminated region. The influence of diffusion on current was shown to be significant.

1. Introduction

Impressed-current cathodic protection systems are used in conjunction with organic coatings on pipelines and other metallic structures to provide protection in regions where the coating has been damaged [1]. These systems mitigate the corrosion at exposed metal surfaces, also known as coating holidays, by driving cathodic reactions such as oxygen reduction and hydrogen evolution. One criterion for cathodic protection implementation involves the maintenance of the pipe surface at a potential more negative than −0.850 V relative to a copper/copper-sulphate reference electrode (or −0.773 V (SCE)). Early cathodic protection models and design equations were developed to account for attenuation to single uniform pipes protected by distant anodes or ground beds [2,3]. Semi-analytic approaches have been developed for cases where the pipe can still be considered to be uniform, but a close anode-to-pipe spacing may cause under-protection of the region of the pipe most distant from the anode while overprotecting the region closest to the anode [4].

The use of boundary element methods to solve cathodic protection problems in infinite media was introduced by Telles et al. [5], Chuang [6] and Zamani et al. [7] employed boundary elements to model cathodic protection of ships. Nisanciglu et al. [8–10] and Santiago and Telles [11] have incorporated time-dependent polarization curves into boundary element models for cathodic protection. Brichau and Deconinck presented a model using boundary element and finite element (FEM) methods for buried pipe networks cathodically protected by anode beds [12]. Their method of surface discretization assumed cylindrical elements (pipe-sections) with a uniform radial current density distribution. The assumption of a uniform current density distribution, however, is valid only for a uniformly coated or fully bare pipeline with a distant anode.

The influence of coating holidays was addressed by Kennelley et al. [13] and Orazem et al. [14] using finite elements. In subsequent work, a more precise boundary-element approach was used to model the role of coating holidays [15,16] for a single pipeline protected by sacrificial ribbon anodes such as those used for the Trans-Alaska pipeline. This model was extended to account for multiple pipelines, multiple CP systems, bonds, and arbitrary anode placement [17–21]. These models show the degree of protection provided to coating holidays which expose bare steel, but the models do not address the influence of the delaminated regions of the coating that often surround holidays.

The delaminated region resembles a crevice in that the electrolyte within is occluded from the exterior bulk environment and electrochemical reactions at any point on the metal surface are influenced by local conditions. Detailed reviews of models for such occluded systems have been presented by Sharland [22] and Turnbull [23]. A model for the steady-state conditions in a disbondment system under cathodic protection was described by Song et al. [24,25]. In this work, the influence of a holiday was not considered.

© 2009 Elsevier Ltd. All rights reserved.
concentration gradients were neglected, and the solution potential was governed by Laplace’s equation. From experimental observations, however, Leng et al. [26,27] and Furbeth and Stratmann [28,29] concluded that cathodic delamination is driven by diffusion of cations within a gel-like region which separates the intact coating and the fully delaminated coating. Their interpretation was supported by simulations developed by Allahar et al. [30] and Huang et al. [31]. Thus, transport of ionic species may be expected to play a critical role in the fully delaminated region as well.

The object of the present work is to explore the potential drop within the delaminated region surrounding a coating holiday in the context of a solution of the coupled equations for conservation of ionic species, including migration and diffusion, and local electroneutrality. This work is intended to elucidate the role of ionic transport within the region in which the coating is fully delaminated. In addition, an expression is sought to relate the potential drop in the delaminated region to parameters which could be accessed by existing CP models. Such an expression could provide a modified boundary condition for CP models to allow estimation of CP requirements for the delaminated region adjacent to a coating holiday.

2. Model development

A schematic representation of a delaminated region surrounding a coating holiday is given in Fig. 1. A cylindrical geometry was assumed with an axis of symmetry centered on the coating holiday. The delaminated region is bounded by the periphery of the holiday and the intact and un-detached coating. The section of metal covered by the intact coating was considered to be fully passivated and did not contribute to the system. The detached coating was considered impermeable to the passage of current and oxygen. When the metal surface is under cathodic protection, current is delivered to the metal surface through the electrolyte in the holiday and delaminated region. The gap between the metal surface and the detached coating was assumed uniform across the length of the delaminated region.

Variable distributions in the direction normal to the metal surface can be considered negligible in the delaminated region far from the holiday [32,33]. The model is developed to take advantage of this feature for deeper portions of the delaminated region. The holiday and the delaminated region was modeled as being a two-dimensional (2-D) domain for positions less than 3 cm and as a one-dimensional (1-D) domain for positions greater than 3 cm. The cut-off at 3 cm was chosen as being the point at which the mass-transfer-limited oxygen reduction current could be considered negligible. The domains were solved individually but coupled at the common boundary between the 2-D and 1-D delaminated region domains using continuity of species concentration, solution potential, and flux of species in the radial direction. Underlined variables $\phi$ and $\phi$ designate the concentration of a species $i$ and the dimensionless solution potential, respectively, in the 1-D domain. No homogeneous reactions were considered. Symbols that are not underlined correspond to the respective variables in the 2-D domain.

The electrolyte in the exterior of the holiday-crevice domain was assumed to contain Na$^+$, Cl$^-$, OH$^-$, and Fe$^{2+}$ ions. The pH was neutral, and the concentration of NaCl was used to vary the resistivity of the electrolyte. An electrolyte composed of $10^{-3}$ M NaCl, $10^{-7}$ M OH$^-$, and $10^{-15}$ M Fe$^{2+}$ corresponded to a resistivity of 7.9 kΩ cm. The applied potential $\Psi$ represents the potential of the metal such that the solution potential at the mouth of the holiday had a value of 0 V(SCE).

2.1. Electrochemical reactions

The electrochemical reactions considered were iron dissolution

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (1)$$

oxygen reduction

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (2)$$

doxygen reduction

$$\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2e^- \quad (3)$$

The current densities for iron dissolution $i_{\text{Fe}}$, oxygen reduction $i_{\text{O}_2}$, and hydrogen evolution $i_{\text{H}_2}$ were given by

$$i_{\text{Fe}} = 10^{0.237 - \frac{E}{295}}$$

$$i_{\text{O}_2} = 10^{0.237 - \frac{E}{295}}$$

and

$$i_{\text{H}_2} = 10^{0.237 - \frac{E}{295}}$$

respectively, where anodic reactions have a positive current density and cathodic current densities have a negative value.

In these equations the interfacial potential $V$ was given by the potential driving the electrochemical reaction $\Psi - \Phi$ where $\Phi$ is the solution potential of a reference electrode located adjacent to the metal surface and $\Psi$ the potential of the metal, also referred to as the applied potential.

The value of the mass-transfer-limited current density $i_{\text{lim,0}_2}$ was calculated as a function of position along the metal surface of the holiday-delaminated region 2-D domain. The contribution of oxygen reduction for positions along the metal surface of the 1-D delaminated region domain was assumed to be negligible when compared to the contribution of hydrogen evolution.

The net current density $i_{\text{net}}$ for steel was given by the sum of the current densities due to the individual electrochemical reactions [34]. Along the metal surface of the holiday and within the 2-D domain of the delaminated region, the value of $i_{\text{net}}$ was given by the sum of $i_{\text{O}_2}, i_{\text{H}_2}$, and $i_{\text{Fe}}$. Along the metal surface of the 1-D domain of the delaminated region, the value of $i_{\text{net}}$ was given by the sum of $i_{\text{O}_2}$ and $i_{\text{Fe}}$. As shown in the subsequent section, the mass-transfer-limited value of the oxygen reduction current became negligible deep within the delaminated region. The Tafel parameters $b_{\text{O}_2}, b_{\text{H}_2}$, and $b_{\text{Fe}}$ used in the polarization expressions for $i_{\text{O}_2}, i_{\text{H}_2}$, and $i_{\text{Fe}}$ were 62.6, 66.5, and 132 mV/decade, respectively. The equilibrium parameters $E_{\text{Fe}}, E_{\text{O}_2}$, and $E_{\text{H}_2}$ were assigned values of $-475$, $-500$, and $-870$ mV(SCE), respectively. These parameters were obtained by fitting polarization curves to experimental data for a slit-holiday [34].
2.2. Oxygen distribution

Under the assumptions that radial symmetry applied and that convection could be neglected, the mass-transfer-limited current density for oxygen reduction $i_{lim,O_2}$ could be obtained by solution of

$$\frac{1}{T} \frac{\partial c_{O_2}}{\partial t} + \frac{\partial^2 c_{O_2}}{\partial r^2} + \frac{\partial^2 c_{O_2}}{\partial z^2} = 0$$

(7)

The boundary condition at the mouth of the holiday was that the concentration was equal to the bulk value, i.e., $c_{O_2} = c_{O_2,\infty}$. No-flux conditions applied at the axis of symmetry ($r = 0$) and along the surface of the detached coating, i.e., $N_{O_2, r} \cdot n = 0$ where $N_{O_2, r}$ is the flux of oxygen and $n$ is the unit vector normal to the surface. As the flux tended toward zero deep within the delaminated region, a no-flux condition was assumed to apply at the boundary between the 2-D and 1-D domains. The boundary condition at the metal surface was $c_{O_2} = 0$ under the assumption that oxygen was reduced completely at the metal surface.

A finite difference method was employed to solve Eq. (7) subject to the respective boundary conditions, and the value of $i_{lim,O_2}$ on the metal surface was calculated using

$$i_{lim,O_2} = nFD_{O_2} \frac{\partial c_{O_2}}{\partial z}$$

(8)

where $n = 4$ is the number of electrons transferred in the electrochemical oxygen reduction reaction per molecule of oxygen $O_2$ (see Eq. (2)), $F$ is Faraday’s constant, and $D_{O_2}$ is the diffusion coefficient of oxygen.

The distribution of $i_{lim,O_2}$ on the metal surface obtained as a solution to Laplace’s equation for $c_{O_2}$ is shown in Fig. 2 for a holiday of radius 0.25 cm, a delaminated region of 1.25 cm, and a gap of 0.05 cm. The value of $i_{lim,O_2}$ was approximately constant at 31 $\mu$A/cm$^2$ along the holiday metal surface and decreased exponentially along the disbondment metal surface such that at a position of 0.5 cm, the value of $i_{lim,O_2}$ was three orders of magnitude less than at the holiday surface. The distribution of $i_{lim,O_2}$ used in the present work was consistent with the results of the mathematical model developed by Chin and Sabde [35,36]. The large exponential decrease in $i_{lim,O_2}$ corresponded to an exponential decrease in the concentration of oxygen within the disbondment. Depletion of oxygen within the disbondment was observed in both experimental studies [37] and mathematical models [24]. The exponential decrease in the value of $i_{lim,O_2}$ with distance in the delaminated region supported the assumption that the influence of oxygen reduction for positions greater than 3 cm was negligible.

2.3. Mathematical model

Conservation of species $i$ yields [38]

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + R_i$$

(9)

where the term on the left-hand-side represents the rate of change of concentration $c_i$ with time $t$ (accumulation) and the terms on the right-hand-side represent the net input due to the flux $N_i$ and the net rate of production by homogeneous reactions $R_i$, respectively. In dilute electrochemical systems $N_i$ is given by the Nernst-Planck equation [38].

$$N_i = -z_i u_i c_i F \nabla \phi - D_i \nabla c_i + c_i z_i u_i$$

(10)

where $\phi$ is the local solution potential, $u_i$ is the mobility, $D_i$ is the diffusion coefficient, $z_i$ is the charge number and $v$ is the mass average velocity of the electrolyte. The terms on the right-hand side of Eq. (10) represent the contributions by migration, diffusion, and convection to the flux of a species, respectively.

The local current density is given by

$$i = F \sum_i z_i N_i$$

(11)

Combination of Eqs. (10) and (11), in the absence of convection, yields

$$i = -k \nabla \phi - F \sum_i z_i D_i \nabla c_i$$

(12)

where the conductivity $\kappa$ is defined as

$$\kappa = \frac{F^2}{RT} \sum_i z_i^2 D_i c_i$$

(13)

The ionic current density has contributions from migration $i_m$ and diffusion $i_d$ [39]. These are the first and second terms, respectively, on the right-hand side of Eq. (12).

Under the assumption of a steady state, conservation of species yields

$$0 = D_i z_i c_i \nabla^2 \phi + D_i z_i \nabla c_i \cdot \nabla \phi + D_i \nabla^2 c_i$$

(14)

in which homogeneous reactions and convection were not considered. In Eq. (14), the dimensionless potential $\phi$ was given by $\phi = (\Phi F) / (R_T T)$ using the Nernst-Einstein equation $D_i = u_i R_T T$, where $R_T$ and $T$ are the molar gas constant and temperature, respectively. The system was modeled using cylindrical coordinates. The governing equations consisted of four equations of the form of Eq. (14), one for each specie, and an algebraic expression for the electroneutrality condition given by

$$z_{Na^+} C_{Na^+} + z_{Cl^-} C_{Cl^-} + z_{OH^-} C_{OH^-} + z_{Fe^{2+}} C_{Fe^{2+}} = 0$$

(15)

Variables $c_i$ and $\phi$ were fixed at the holiday mouth to the bulk conditions $c_{i,\infty}$ and $\phi_{\infty}$, respectively. The solution potential $\phi_{\infty} = 0$ was used such that the calculated values for $\phi$ in the model were referenced to a zero value at the bulk boundary position. The condition of electroneutrality was applied at all boundaries, and a no-flux condition $N_i \cdot n = 0$ was applied at all insulating boundaries.

Flux conditions were applied at the metal surface. The no-flux condition was used for the chemically inert species Na$^+$ and Cl$^-$. The flux conditions for OH$^-$ and Fe$^{2+}$ were related to the current densities due to the cathodic ($i_{lim}$ and $i_{\alpha}$) and anodic ($i_{\beta}$) electrochemical reactions on the metal surface, respectively, as

$$-z_{Fe^{2+}} D_{Fe^{2+}} \frac{\partial \phi}{\partial z} - D_{Fe^{2+}} \frac{\partial C_{Fe^{2+}}}{\partial z} = \frac{i_{\beta}}{2F}$$

(16)
When the delaminated region was smaller than 3 cm, the no-flux conditions and electroneutrality were applied at the intact boundary. For delaminated regions larger than 3 cm, the condition on the common boundary between the 2D-delaminated region and 1D-delaminated region was a flux condition given by

$$-z_i D_i \frac{\partial i}{\partial r} - D_i \frac{\partial i}{\partial r} = N'_i$$

where $N'_i$ was the flux in the $r$-direction at the boundary in the 1-D delaminated region. The value of $N'_i$ was given by

$$N'_i = -z_i D_i \frac{\partial i}{\partial r} - D_i \frac{\partial i}{\partial r}$$

where $c^i$ and $\phi^i$ were the concentration of a species $i$ and the dimensionless solution potential in the 1-D delaminated region on the common boundary.

2.4. One-dimensional delaminated region

The conservation equation for species $i$ in a dilute environment given by Eq. (14) was cast to a 1-D domain in cylindrical coordinates to give

$$0 = -1 \left[ \frac{d(rN)}{dr} \right] + S$$

where $N$ was the flux of a species $i$ in the $r$-direction and $S$ the production of species from electrochemical reactions from the domain region $r$. The term $S = 0$ for the chemically inert species Na$^+$ and Cl$^-$ that did not participate in electrochemical reactions. For the reacting species Fe$^{2+}$ and OH$^-$. The percentage contributions of $i_{\text{r,d}}$ to the radial current density was uniform for the bulk as a parameter. For a given applied potential, the percentage of $i_{\text{r,d}}$ was approximately 55% for the three applied potentials. The percentage contributions of $i_{\text{r,d}}$ to the radial current density was approximately 55% for the three applied potentials.

The percentage contribution of $i_{\text{r,d}}$ to the radial current density was approximately 55% for the three applied potentials. The percentage contribution of $i_{\text{r,d}}$ to the radial current density was a function of position in the delaminated region is shown in Fig. 3(b) with applied potential as a parameter. The current density had a positive value in the delaminated region as current was supplied to the metal surface. The variations of $i_{\text{r,d}}$ with position were similar for the three applied potentials. This was because hydrogen evolution became more significant with more negative applied potentials. Also, for a given bulk electrolyte resistivity and at a given position in the delaminated region, a change to a more negative applied potential resulted in increases in the absolute values of $i_{\text{r,d}}$ and the contribution due to migration $i_{\text{m}}$. The percentage contribution of $i_{\text{r,d}}$ to $i_r$, as a function of position in the delaminated region is shown in Fig. 3(b) with applied potential as a parameter. For $r > 1.225$ cm the $i_{\text{r,d}}$-contributions is not included as $i_r$ approached a zero value due the no-flux condition for $c_i$ at the coating boundary, $r = 1.25$ cm. The variations of the contributions of $i_{\text{r,d}}$ are shown in Fig. 3(b) with applied potential as a parameter. The current density had a positive value in the delaminated region as current was supplied to the metal surface. The variations of $i_{\text{r,d}}$ with position were similar for the three applied potentials. For a given applied potential, the value of the $i_{\text{r,d}}$-contribution decreased with position in the delaminated region and approached an asymptotic value. The asymptotic values for the applied potentials were 45 to 52% indicating that the contribution of $i_{\text{r,d}}$ to the transport in the delaminated region was significant for the applied potential range. At the entry to the delaminated region the $i_{\text{r,d}}$-contribution was approximately 55% for the three applied potentials.

3. Numerical method

The linearized governing equations for species mass-transfer and electroneutrality were discretized using second-order difference approximations. The resulting non-linear systems of equations were solved using an iterative method. The mathematical model was developed using Compaq Visual Fortran, Version 6.1 with double precision accuracy. The algorithm is described in reference [32]. In all the simulations grid spacings of $\delta r = 0.025$ cm and $\delta z = 0.0125$ cm were used in the radial and axial directions, respectively. The boundary radius and delaminated region gap were fixed at 0.25 cm and 0.05 cm, respectively. The convergence criterion for the iterative algorithm was 0.01%. The assumed values of diffusion coefficients were $D_{\text{Fe}} = 1.3341 \times 10^{-5}$ cm$^2$ s$^{-1}$, $D_{\text{Cl}} = 2.0344 \times 10^{-5}$ cm$^2$ s$^{-1}$, $D_{\text{OH}} = 5.2458 \times 10^{-5}$ cm$^2$ s$^{-1}$, and $D_{\text{H}} = 0.7172 \times 10^{-5}$ cm$^2$ s$^{-1}$ [40]. The assumed value of $D_0 = 2.92 \times 10^{-5}$ cm$^2$ s$^{-1}$ corresponded to the diffusion coefficient in dilute NaCl solution [41].

4. Results

The model results were used to elucidate the role of ionic transport within the region in which the coating is fully delaminated. In addition, an expression was developed to relate the potential drop in the delaminated region to parameters which could be accessed by existing CP models.

4.1. Contribution of diffusion transport in delaminated regions

The axial variation of potential and concentration in the delaminated region was negligible, and the dominant component of current density was in the radial direction. The percentage contribution of the radial diffusion component of current density to the total radial component, i.e., $i_{\text{r,d}}/i_r$, was used as a measure of the importance of diffusion transport.

The distribution of the radial component of current density in a 1 cm deep delaminated region is shown in Fig. 3(a) with applied potential as a parameter. The current density had a positive value in the delaminated region as current was supplied to the metal surface. The variations of $i_{\text{r,d}}$ with position were similar for the three applied potentials. The value of $i_r$ decreased with position approaching a zero-value as the intact boundary was approached. For a given position in the delaminated region, larger values of $i_{\text{r,d}}$ were associated with more negative applied potentials. This was because hydrogen evolution became more significant with more negative applied potentials. Also, for a given bulk electrolyte resistivity and at a given position in the delaminated region, a change to a more negative applied potential resulted in increases in the absolute values of $i_{\text{r,d}}$ and the contribution due to migration $i_{\text{m}}$. The percentage contribution of $i_{\text{r,d}}$ to $i_r$, as a function of position in the delaminated region is shown in Fig. 3(b) with applied potential as a parameter. For $r > 1.225$ cm the $i_{\text{r,d}}$-contributions is not included as $i_r$ approached a zero value due the no-flux condition for $c_i$ at the coating boundary, $r = 1.25$ cm. The variations of the contributions of $i_{\text{r,d}}$ are shown in Fig. 3(b) with applied potential as a parameter. The current density had a positive value in the delaminated region as current was supplied to the metal surface. The variations of $i_{\text{r,d}}$ with position were similar for the three applied potentials. For a given applied potential, the value of the $i_{\text{r,d}}$-contribution decreased with position in the delaminated region and approached an asymptotic value. The asymptotic values for the applied potentials were 45 to 52% indicating that the contribution of $i_{\text{r,d}}$ to the transport in the delaminated region was significant for the applied potential range. At the entry to the delaminated region the $i_{\text{r,d}}$-contribution was approximately 55% for the three applied potentials.

The bulk electrolyte provided the boundary conditions for the composition at the mouth of the holiday. The distribution of the radial ionic current density in a 1 cm disbondment is shown in Fig. 4(a) with bulk resistivity as a parameter. The distributions of $i_r$ were similar for the 79 k$\Omega$ cm and 0.79 k$\Omega$ cm bulk resistivities were similar to that of 7.9 k$\Omega$ cm bulk resistivity that was discussed. For a given position in the delaminated region, larger values of $i_r$ were associated with smaller resistivities. The percentage contributions of $i_{\text{r,d}}$ to the radial current density as a function of position are shown in Fig. 4(b) with bulk resistivity as a parameter. For the bulk resistivity of 7.9 k$\Omega$ cm, the $i_{\text{r,d}}$-contribution decreased with position with the overall decrease being approximately 5%. The $i_{\text{r,d}}$-contributions was uniform for the bulk resistivities of 0.79 and 79 k$\Omega$ cm for positions greater than 0.29 cm. For positions ranging from 0.25 cm to 0.29 cm, the value of $i_{\text{r,d}}$ decreased by less than 2%. Therefore, the relative contributions of the diffusion current density to the ionic current density...
was approximately uniform except for a maximum change of 5% at a bulk resistivity of 7.9 kΩ cm. For a given position in the delaminated region, larger relative contributions of the diffusion current were associated with smaller bulk resistivities. This was consistent with the theory of supporting electrolytes, where the effect of migration was reduced with decreased resistivity [38].

The distribution of the radial ionic current density $i_r$ in the disbondment is shown in Fig. 5(a) with disbondment length as a parameter. The variations of $i_r$ with position were similar for the different disbondment lengths. The value of $i_r$ decreased with position and approached a zero value as the disbondment tip was approached. For a given position in the disbondment that was common between two distributions, a larger value of $i_r$ was associated with the longer delaminated region. This was because a larger cathodic current on the metal surface was associated with the longer delaminated region.

The relative contribution of $i_{rd}$ to $i_r$ in the delaminated region are shown in Fig. 5(b) with delaminated region length as a parameter. The variation of the $i_{rd}$ contribution for the 2 and 3 cm disbondments were similar to the corresponding variations for the 1 cm delaminated region. For a position common between two distributions, a smaller value of the $i_{rd}$-contribution was associated with the longer delaminated region. This demonstrated that the contribution of diffusion in the delaminated region was reduced with delaminated region length. However, the $i_{rd}$-contribution was still significant, especially over the first 1 cm into the delaminated region.
4.2. Potential distribution in the delaminated region

Results from the model were used to develop an expression for the potential drop as a function of delaminated region length and bulk resistivity for a given applied potential. The concentrations of the bulk NaCl used were approximately 0.01, 0.005, 0.001, 0.0005, 0.0002, and 0.0001 M. These corresponded to bulk resistivities of 0.79 1.58, 7.9, 15.8, 39.5, and 79 kΩ cm, respectively. The applied potential used in the simulations was $-0.773$ V(SCE), similar to a criterion used for the implementation of impressed-current cathodic protection.

The distributions of solution potential and local electrolyte resistivity, expressed as a percentage of the bulk resistivity, are shown in Fig. 6(a) and (b), respectively, with delaminated region length as a parameter for a bulk electrolyte resistivity of 0.79 kΩ cm. The distributions of solution potential were similar for the different lengths, with a more negative value of the potential at the innermost part of the delaminated region, the intact boundary, associated with a longer delaminated region. The distributions of local electrolyte resistivity were also similar with a smaller local electrolyte resistivity at the intact boundary associated with a longer delaminated region.

The model results were used to calculate the potential drop across the delaminated region and the resistivity at the boundary between the delaminated and intact regions. These values are presented in Fig. 7(a) and (b), respectively, as functions of delamination depth with bulk resistivity as a parameter. For a given bulk resistivity, larger solution potential drops and smaller local electrolyte resistivities were associated with longer delaminated regions. For a given delaminated region length, larger solution potential drops were associated with larger bulk resistivities. The change in the local electrolyte resistivity was larger for larger bulk electrolyte resistivities for a given delaminated region length.

The potential drop across the delaminated region is seen to be a function of the delaminated region length and bulk resistivity. A design equation was developed for conditions of a 0.5 cm holiday radius, 0.05 cm gap size, 0.05 cm coating thickness, and a metal potential of $-0.773$ V(SCE) relative to a zero value of solution potential at the mouth of the holiday.

The equation of a distribution was assumed of the form

$$
\Phi = a_1 + \frac{a_2}{1 + \exp[(a_3 - r_0)/a_4]}
$$

where $a_1$, $a_2$, $a_3$, and $a_4$ were design parameters. The values of these design parameters were obtained by fitting by inspection the distribution to the model-calculated values. The values of the design parameters are given in Table 1.

The value of $\Phi$ as a function of delaminated region length with bulk resistivity as a parameter calculated using these design parameters and Eq. (23) are shown in Fig. 8 as dashed lines. There was a good correlation between the model-calculated (symbols) and equation-calculated (dashed lines) values for $\Phi$.

The design parameters are shown as functions of the bulk resistivity in Fig. 9. To include an explicit dependence of Eq. (23) on resistivity, the expression

$$
a_k = p_k \ln(\rho_\infty) + q_k
$$

was fitted to each parameter where $p_k$ and $q_k$ were fitting parameters for the design parameters $a_k$. The values of the fitting parameters, obtained using Microsoft Excel, were $p_1 = 2.1715$ mV, $q_1 = 4.1785$ mV, $p_2 = -10.857$ mV, $q_2 = -52.559$ mV, $p_3 = -1.32$ 46 cm, $q_3 = 5.8378$ cm, $q_4 = -0.1954$ cm, and $q_4 = 2.6706$ cm.

The expression for the solution potential drop in the delaminated region was

$$
\Phi(r_0, \rho_\infty) = a_1(\rho_\infty) + \frac{a_2(\rho_\infty)}{1 + \exp[a_3(\rho_\infty) - r_0]/a_4(\rho_\infty)\ln(\rho_\infty)}
$$

where the design parameters were functions of bulk resistivity in kΩ cm given by Eq. (24). The value of the $\Phi$ as a function of delaminated region length is shown in Fig. 8 with bulk electrolyte resistivity as a parameter. The values of model-calculated $\Phi$ are shown together with the fits of Eq. (23) and the design-equation-calculated values of Eq. (25). There was agreement between the values of $\Phi$ calculated using the design equation and the model.

5. Discussion

Many mathematical models of pitting and parallel-sided systems have been presented in the literature that calculate the steady-state and transient conditions within the occluded domain. These include the hemispherical pitting system [42–46], the parallel-sided delaminated region with an active tip and passive walls [47–53] and the parallel-sided delaminated region with active walls [54,47,53,55–59]. Very few models presented in the literature, however, address the coupling between the holiday and a delaminated region.

The assumptions used in constructing the models presented in literature for holiday/delaminated-region systems and delaminated-region systems were aimed at reducing the complicity of the system. In one model for a circular delaminated region surrounding a holiday, only oxygen reduction was considered significant and the diffusion coefficients of the species were equated to eliminate the coupling of the governing equations for concentration and solution potential [35,36]. In the transient model for a rectangular holiday with a delaminated region adjacent to one side, elec-

Fig. 6. Calculated (a) solution potential and (b) local electrolyte resistivity as functions of position on the metal surface with delaminated region length as a parameter for bulk electrolyte resistivity of 0.79 kΩ cm. The dashed line at $r = 0.25$ cm indicates the boundary between the holiday and the delaminated region.
Models of a delaminated region adjacent to a holiday have been presented where the influence of the holiday was not considered. A method involving control volumes was developed for a transient model for the conditions of the one-dimensional delaminated region system [61]. Song et al. assumed the concentration gradients in the delaminated region were negligible and the solution potential was governed by Laplace’s equation [24,25]. Another model was presented where the holiday was considered and a two-dimensional solution was obtained [62,63].

The present model calculated the steady-state electrolyte composition in the holiday/crevice system while accounting for the presence of a holiday, transport by diffusion and migration, and relevant cathodic and anodic electrochemical reactions. The model was used to demonstrate that the influence of diffusion was significant for the ±50 mV range about the −0.730 V criterion, for the bulk resistivity ranging from 0.79 to 79 and for any delaminated region length. The influence of diffusion was seen to be the greatest at the entry of the delaminated region from the holiday. These results demonstrated that the commonly used assumption that concentration gradients can be neglected in the delaminated region is not valid. The interpolation formula presented as Eq. (25) provides an approach for representing the simulation results while accounting for the resistivity of the environment exterior to the holiday and the length of the delaminated coating. The expression used requires assumption of a fixed delamination gap thickness, a fixed holiday size, and a fixed applied potential. These limitations can be alleviated by using the model and the approach outlined to develop analogous expressions.

Future extensions to this work should account for the permeability of the coating to dissolved gases and ionic species, homogeneous reactions such as dissociation of water and ferrous ion hydrolysis, pH-dependence of electrochemical reactions, and use of concentrated rather than dilute solution expressions for transport phenomena. Inclusion of these phenomena may be expected to yield competing influences on the estimated variation of potential within the delaminated region. Local increases in pH will result in reduced electrical current associated with the hydrogen evolution reaction [55]; whereas, transport of oxygen through a permeable coating will increase the oxygen reduction current. Rouw observes, however, that the barrier property of organic coatings alone is not sufficient to prevent corrosion and that the most significant contribution of a coating to the mitigation of corrosion arises from the reduction of the rates of transport of ionic species [64]. Inclusion of coating permeability to ionic species will tend to reduce the variation of potential associated with large concentration gradients. It should be noted that the species included in the present model were the dominant species needed for calculation of electrolyte resistivity. Addition of H⁺ and Fe(OH)⁺ concentrations as variables would not contribute significantly to the resistivity. Thus, inclusion of H⁺ and the water dissociation reaction would improve the pH calculation in the delaminated region, but would have minimal impact on the electrolyte resistivity.

While, as described above, refinements to account for homogeneous reactions and coating permeability are desirable, the present work serves the useful purposes of illustrating the importance of changes in local composition within the delaminated region and
of providing a means for modifying existing CP programs to estimate the potential underneath delaminated regions.

6. Conclusions

A mathematical model was presented for the steady-state conditions in a delaminated region surrounding a circular holiday on a metal surface under cathodic protection. Oxygen reduction and distributions normal to the metal surface were found to be negligible for delaminated regions greater than 3 cm. The results demonstrate that the commonly employed assumption that concentration gradients are negligible is not valid within the delaminated region. The results from the model were used to construct an expression for the potential drop in a holiday-delaminated region system as a function of bulk resistivity and delaminated region length for a given applied potential. The expression can also be used to estimate the potential drop from the bulk to the holiday metal surface in the absence of a surrounding delaminated region. This expression can be used in conjunction with existing CP models to refine estimates for the potential requirement of an impressed-current system.

Acknowledgements

This work was supported by the Gas Research Institute through Grant 5097-260-378. The authors acknowledge the contribution of Dr. N. Sridhar at the Center for Nuclear Waste Regulatory Analysis, Southwest Research Institute, San-Antonio, Texas.

References
