ABSTRACT

Current distribution and surface structure were studied for an iron disk in 1M sulfuric acid subjected to a uniform axial velocity at potentials cathodic to the passivation potential. The surface of the electrode was transformed from a granular to a smooth surface at potentials at which the current was observed to oscillate. The smooth surface was seen initially at the periphery of the electrode and grew inward toward the center of the disk as the potential was increased. In contrast to data obtained for partially passivated electrodes, the rate of corrosion was higher at the outside of the disk than in the center. These observations are attributed to the radial distribution of the potential driving force for the corrosion reaction and to the formation of a salt film. Current oscillations are seen on the region of the electrode covered by the salt film. This explanation is supported by a mathematical model which treats the radial variation of current density, potential driving force for corrosion, and concentration of ferrous ions adjacent to the electrode surface. Excellent agreement is obtained with the experimental results.

A uniform solution potential and a uniform current distribution cannot coexist on a disk electrode (1, 2). This consequence of the disk geometry is significant for the corrosion of iron disks in sulfuric acid because the current densities are large. Law (3) and Law and Newman (4) showed that the radial distribution of potential difference near the passivation potential is associated with the cyclic formation, growth, and dissolution of the salt film. Current oscillations were seen on an iron disk before the passivation potential is reached. Their mathematical model provided good agreement with the experimental results of Epelboin et al. (5) and supported the conclusion that the hysteresis observed in current-potential curves for this system can be attributed to the potential drop between the solution adjacent to the electrode and the reference electrode. Russell and Newman (6) provided experimental verification of this result through their investigation of current-potential curves for disks of different radii. Another result of the model of Law and Newman (3, 4) was that iron disks held at potentials for which the iron electrode is partially passivated should corrode preferentially in the center. The outer ring of the disk, in this case, is protected by a passive layer. Russell and Newman (6) observed preferential corrosion of the center of iron disks held at potentials for which the iron is partially passivated. Epelboin et al. (5), however, observed three distinct cases: preferential corrosion at the center of the disk, preferential corrosion in an outer ring, and preferential corrosion of both a central disk and an outer ring with an inner ring subject to lower rates of corrosion.

A number of workers have concluded that the passivation of iron in sulfuric acid is preceded by the formation of a ferrous sulfate film (7-14). This film may be a hydrated ferrous salt. There is evidence that the oscillations in current observed on an iron disk before the passivation potential are associated with the cyclic formation, growth, and dissolution of the salt film (12-14). Russell (15) and Russell and Newman (16) presented results of a mathematical model based upon this mechanism which show the oscillations observed in the current-potential curve near the passivation potential. The salt film provides a barrier to the diffusion of hydrogen and ferrous ions and suppresses the corrosion reaction such that as the salt film grows, both the concentration of ferrous ions adjacent to the surface and the current decreases. The pH of the solution adjacent to the iron surface was found to change as a result of the growth and dissolution of the film. These oscillations have also been explained through application of bifurcation analyses (17, 18). The influence of fluid velocity on the formation of a salt film was investigated by Alkire and Cangellari (19) for high velocity flow between parallel-plate electrodes. They concluded that a sufficiently high flow rate could prevent repassivation of the iron surface. Their experimental results were supported by a mathematical model (19) which treated convective diffusion and the potential field distribution near the dissolving electrode. Their work indicated that repassivation occurred at flow conditions which permitted formation of a ferrous sulfate salt film on at least part of the electrode surface. At sufficiently high flow rates, the surface concentration is too low to permit precipitation of the metal salt, and the dissolving metal does not passivate.

This work presents the current distribution and changes to the surface structure of an iron disk subject to a uniform axial velocity at potentials cathodic to the passivation potential. Experiments were conducted with an impinging electrolyte jet [see Ref. (20-24)] in 1M sulfuric acid. The velocity in the axial direction for this system is uniform under geometric constraints outlined by Chinn and Tsang (20). The results of the experiments are explained with the aid of a mathematical model, based on the work of Newman (1), Law (3), and Law and Newman (4), which treats the radial variation of current density, potential driving force for corrosion, and concentration of ferrous ions adjacent to the electrode surface.

Experimental Study

The experimental method and results are presented in this section. A more detailed description of the experimental method is given by Miller (22).

Method.—The experimental design for the impinging electrolyte jet system is shown in Fig. 1. The electrode has a 99.9985% iron disk embedded in an insulating epoxy disk. The radius of the electrode was 0.249 cm. The reference electrode was a saturated calomel electrode which was separated from the main cell by a glass frit to avoid contamination of the electrolyte by chloride ions. The solution was sparged with nitrogen in 1M sulfuric acid. The velocity in the axial direction for this system is uniform under geometric constraints outlined by Chinn and Tsang (20). The results of the experiments are explained with the aid of a mathematical model, based on the work of Newman (1), Law (3), and Law and Newman (4), which treats the radial variation of current density, potential driving force for corrosion, and concentration of ferrous ions adjacent to the electrode surface.

Results.—The electrochemical experiments included measurement of current-potential curves under several
fluid velocities, measurement of current-time curves for potentials stepped from -1.0V (SCE) to potentials near the passivation potential, EDX analysis of the resulting electrodes, and optical and electron microscopy of the electrodes.

Current-potential curves.—Current-potential curves, presented in Fig. 2, were obtained at a sweep rate of 20 mV/s for jet speeds of 0.10, 0.34, and 1.05 m/s. The potential was swept from -1.0 to +1.0V referenced to the saturated calomel electrode located in a side chamber. Oscillations in the current were observed near the passivation potential. Also near the passivation potential, the metal surface underwent a change in structure. At the beginning of the sweep, a rough granular surface was produced. Just prior to passivation, however, a very uniform and smooth surface was observed. As the potential was increased, the smooth region appeared initially at the periphery of the electrode and propagated inward toward the center of the disk until the entire electrode was smooth. Passivation took place at higher potentials. The radial dependence of the transition from a granular to a smooth surface can be discerned clearly at sweep rates less than 0.5 mV/s, and the range of potentials associated with this transition corresponds to the potential range for which the oscillations in the current were first observed. These observations are similar to those reported by Beck (14) who observed the formation of a salt film that initially precipitated at the periphery of a shielded iron electrode and spread inward toward the center. The transition region was studied through potential-step experiments presented in the following section.

Potential-step experiments.—The time-dependent current is presented in Fig. 3 for a disk subjected to a 1.05 m/s velocity jet and to an instantaneous potential change from -1V to an anodic potential of 0.62V (SCE). The corresponding current-potential curve obtained with a 20 mV/s sweep rate is given as curve b in Fig. 2. Similar results were obtained for potentials anodic to +0.3V; however, the amplitude of the oscillations increased at higher potentials as seen in Fig. 2. The electrodes were held at the anodic potential for three minutes; the first sixty seconds and the last ten seconds were recorded.

The current presented in Fig. 3 approaches a steady-state value within 30s which implies that the system is in an unsteady state for most of the current-potential curve obtained with a 20 mV/s sweep rate.

A series of these potential-step experiments for a constant jet speed provided steady-state information for specific points on the current-potential curve. Photographs of the electrode surfaces are shown in Fig. 4 for anodic potentials of +0.30, +0.55, and +0.62V at a jet speed of 1.05 m/s. The transition from a granular to a smooth surface proceeded radially inward with increasing potential. At +0.30V the disk is dominated by granular corrosion with only the outer edge being smooth. The electrode was bowl shaped after corrosion at +0.62V.

The profiles of the electrodes were obtained by a depth of field technique with a Zeiss inverted-stage optical mi-

Fig. 1. Schematic representation of the experimental cell incorporating an impinging-jet electrode.

Fig. 2. Measured current as a function of electrode potential referenced to a saturated calomel electrode with jet velocity as a parameter: (a) 1.05 m/s, without deaeration; (b) 1.05 m/s deaerated with nitrogen for 2h; (c) 0.34 m/s, deaerated; (d) 0.10 m/s, deaerated.

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The profiles of the electrodes were obtained by a depth of field technique with a Zeiss inverted-stage optical mi-

Fig. 3. Measured current as a function of time for an iron electrode subjected to a 1.05 m/s jet of deaerated 1M sulfuric acid. The potential was stepped from -1.0V to +0.62V (SCE) and held for three minutes.

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sis was performed. The low magnification micrograph shown in Fig. 6a shows an overview of the transition from the granular central region to the smooth outer region. A higher magnification micrograph of the transition between the granular and smooth region is given in Fig. 6b. This micrograph shows that the change between the granular and smooth regions is abrupt and occurs roughly in the center of the micrograph. The surface roughness of the granular region, shown in Fig. 6c, is due to preferential corrosion at the grain boundaries.

Electron micrographs for an electrode held at a more anodic potential [+0.62V (SCE)] are presented in Fig. 7. Figure 7a provides an overview of most of the surface. The electrode was mostly smooth with a small granular region at the center. A micrograph of the granular region is given as Fig. 7b. The micrograph of the uniform region (Fig. 7c) shows a surface pattern which may be associated with a film. Analysis of this region by EDX indicated the presence of an iron oxide layer which was not detected on the granular surface.

Mathematical Model

A mathematical model, presented in Appendix A, was used to explain the experimental results presented in the preceding section. This model treats the coupled effects of the radial dependence of the potential of the solution adjacent to the electrode, the concentration of ferrous ions adjacent to the electrode, the current density on the electrode, and mass transfer to and from the electrode. The numerical method is summarized in Appendix B. The development presented in Appendices A and B is based on the work of Newman (1), Law (3), and Law and Newman (4) for rotating disk electrodes. The treatment for the stagnation region of an impinging jet is analogous to that for a rotating disk because the velocity to the disk is independent of radial position.
bution is presented in Fig. 9 and 10 for jet speeds of 0.10 and 1.05 m/s, respectively. The current distribution is uniform at cathodic potentials (-0.5V) and for currents limited by mass transfer (1.1V for a jet speed of 1.05 m/s and 0.5V for jet speeds of 0.1 m/s). At intermediate potentials the disk corrodes preferentially at the outer edge due to a local increase in the potential driving force for corrosion.

The radial distribution of current is associated with a corresponding distribution for the surface concentration of ferrous ions as shown in Fig. 11 and 12. For all potentials, the concentration of ferrous ions at the surface of the electrode is either uniform or greatest at the outside edge of the disk. The concentration distribution is essentially independent of the bulk concentration for bulk ferrous concentrations less than 10^-3M, and the maximum concentration is obtained at the limiting current. The value of the maximum surface concentration is independent of jet velocity because the higher jet velocity enhances mass transfer both to and from the disk. The calculated maximum surface concentration obtained in this study was 3.42M. This value is sensitive to the value of diffusion coefficient, which was set to 0.1658 x 10^-5 cm/s [following Russell and Newman (16)]. The saturation concentration of ferrous ions in 1M sulfuric acid is 1.52M (25); therefore, the surface concentrations obtained in

Fig. 6. Electron micrographs of the electrode surface held at a potential of +0.5V (SCE) and subjected to a 1.05 m/s jet. a) Overview of electrode including central granular region and parts of a smooth region; b) transition from a granular to a smooth surface; and c) central granular region.

Discussion

Comparison between the model calculations and the experimental results shows that the ring formation, observed at potentials where current oscillations are also observed, can be attributed to formation of a ferrous sulfate salt film. The experimental current distribution, as determined by the electrode profiles, support the hypothesis that local current oscillations take place on the region of the electrode covered by the salt film.

Formation of a salt film.—The calculated average current density on the disk electrode is presented in Fig. 8 as a function of the disk potential referenced to a saturated calomel reference electrode with the hydrodynamic constant (see Eq. [A-1b]) as a parameter. The hydrodynamic constant was obtained from comparison of experimental values of the mass-transfer limited current density to a modification of the Levich equation [see Ref. (20)]. Independent measurement of mass-transfer limited currents on ring electrodes has also been used to obtain the hydrodynamic constant (24). The results presented in Fig. 8 are equivalent to those obtained by Law and Newman (3, 4) for the rotating disk electrode with the exception that the passivation of the electrode is not included. This extension would follow Law and Newman (3, 4) but is not needed for this work because the precipitation of the salt film precedes passivation. The radial current distribu-
Fig. 8. Calculated average current density as a function of electrode potential referenced to a saturated calomel electrode with hydrodynamic constant as a parameter. Dashed lines are for the reference electrode located at infinity and solid lines are corrected for the location of the reference electrode used in the experimental study.

These calculations are well within the range for which precipitation of a ferrous salt film is to be expected.

The radial distribution of surface concentration of ferrous ions suggests that a ferrous salt film forms on the electrode at anodic potentials, extending radially inward with increasing electrode potential. A radius of transition was defined to be the radius of granular corrosion such that \( r_t = r_o \) if the entire disk experiences granular corrosion and \( r_t = 0 \) if the entire disk corrodes smoothly. The radius of transition was obtained by measuring the average radius for the granular region in photographs such as those presented in Fig. 4. The radius of transition between granular and uniform corrosion is presented in Fig. 13 as a function of potential for jet velocities of 0.1, 0.34, and 1.05 m/s. The transition from granular to smooth corrosion takes place at a more anodic potential at high jet speeds.

Fig. 9. Calculated current distribution on the disk at a jet speed of 0.1 m/s (\( \alpha = 16 \text{ s}^{-1} \)) with cell potential as a parameter.

Fig. 10. Calculated current distribution on the disk at a jet speed of 1.05 m/s (\( \alpha = 147 \text{ s}^{-1} \)) with cell potential as a parameter.

Fig. 11. Calculated surface concentration of ferrous ions on the disk at a jet speed of 0.1 m/s (\( \alpha = 16 \text{ s}^{-1} \)) with cell potential as a parameter.
Comparison between the mathematical model and the experimental results requires determination of the critical concentration for precipitation of a ferrous salt film and adjustment for the effect of the location of the reference electrode relative to the disk electrode. The concentration at which a salt film was presumed to form was obtained by matching the fraction of limiting current \( i_{lim} \) at which the ring effect and the current oscillations were first observed to the calculated current-potential curves given in Fig. 9 to get the disk potential referenced to infinity. The concentration at \( r/r_0 = 1 \) for this potential was obtained for a jet velocity of 1.05 m/s to be 3.11M. This value was independent of jet velocity and is 2.05 times larger than the saturation concentration reported for ferrous ions in 1M sulfuric acid (25). The factor of 2.05 is consistent with the work of Beck (14) who observed supersaturated concentrations of the order of 1.8-2.6 times the saturated value before the onset of salt film formation. The transition radius based upon this concentration is presented by solid lines in Fig. 13 as a function of the electrode potential referenced to the calomel electrode. The actual location of the reference electrode was below the plane of the disk, a position that is undefined in the mathematical solution. An effective location was obtained by matching the solution to the experimental results for the high-speed jet. No additional adjustment was made for the lower velocities.

Current oscillations.—The combined results of Fig. 2 (curve a or b), 4(a), and 5 (curve for \( V = 0.3V \)) indicate that oscillations are not observed when the corrosion occurs with a granular morphology. The oscillations must therefore be associated with the outer portion of the electrode which corrodes while covered by a sulfate salt film. The surface profile shown in Fig. 5 for \( V = 0.30V \) indicates that shielding by the epoxy results in reduced corrosion rates only on a limited region of the electrode between \( r/r_0 = 0.87 \) and \( r/r_0 = 1 \). This appears to be confirmed by sharp breaks in the surface profiles for \( V = 0.55 \) and \( V = 0.62V \) that also occur near \( r/r_0 = 0.87 \). It may also be helpful to think in terms of the aspect ratio formed by dividing the distance away from the metal-oxide boundary in the \( r \)-direction by the depth below the epoxy plane in the \( z \)-direction. This ratio is 2.6 at \( r/r_0 = 0.87 \) and 10 at \( r/r_0 = 0.5 \).

The curve for \( V = 0.55V \) (Fig. 5) shows reduced corrosion rates from \( r/r_0 = 0.87-1.0 \). Assuming that shielding can only account for reduced rates in the region of \( r/r_0 = 0.87-1.0 \), what leads to the reduced corrosion rates between \( r/r_0 = 0.87 \)? One possible answer to this question is the occurrence of periodic passivation and activation of the region under the salt film. The experiments in this work have shown that, at \( V = 0.55V \), a salt film covers the surface from \( r/r_0 = 0.45-1.0 \). The corrosion rate decreased in the region of \( r/r_0 = 0.6-0.87 \) without the influence of shielding. If the influence of a salt film were not considered, the higher potential driving force would lead to increased corrosion rates. Periodic passivation and activation in the region between \( r/r_0 = 0.6-0.87 \) (or to 1.0) would create the observed current oscillations. The time spent in the passivated state would cause the time-averaged corrosion rate on the region between \( r/r_0 = 0.6-0.87 \) to be less than the nearly uniform corrosion rate observed in the region between \( r/r_0 = 0.45-0.60 \). This mechanism for current oscillations is consistent with the results of the one-dimensional time-dependent mathematical model developed by Russell and Newman (15, 16). This hypothesis is also supported by the observation by EDX of an oxide film in the region covered by a salt film at 0.62V (SCE) which was not seen on the granular surface. It is not necessary, however, to assume periodic active/passive cycling. Periodic changes in the salt film porosity or in the exposed area under the salt film could also explain the current oscillations and reduced corrosion rates. Either hypothesis would be consistent with the observation that the amplitude of the current oscillations becomes larger as a larger portion of the disk becomes covered by the salt film.

Conclusions

The mathematical and experimental study presented here provides evidence that current oscillations reported for iron disks in sulfuric acid are observed when a salt film...
film covers the surface. The coupling of the effects of convective diffusion with the variation of potential in the electrolyte causes the precipitation of the salt film on a disk electrode to occur first at the periphery of the disk, extending inward as the potential is increased. This supports the previous work of Beck (14) who also observed the formation of a salt film that initially precipitated at the periphery of an iron electrode and spread inward toward the center. This result has been observed both on a disk subjected to a submerged impinging jet (reported here) and on a rotating iron disk (26). The precipitation of the salt film is accompanied by a change in the electrode morphology from a granular surface to a smooth surface. The salt film acts as a diffusion barrier, making the higher regions more accessible to corrosion and providing a leveling effect. The increased rate of corrosion under the salt film as compared to the center of the disk is caused by the higher potential driving force present at the periphery. Part of the electrode covered by the salt film exhibited reduced corrosion rates, and this observation may be due to periodic active/passive cycling or other periodic changes associated with the salt film.

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APPENDIX A

Theoretical Development

The disk electrode was of finite size and was assumed to be embedded in an infinite insulating plane. The walls of the cell and the counterelectrode were assumed to have no effect on the disk. Dilute-solution theory with constant diffusion coefficients, mobilities, and activity coefficients was assumed to apply.

The Schmidt number $Sc = v/D$ is large in electrolytic solutions, and the concentrations differ from their bulk values in only a thin region near the surface. In this region the fluid velocity can be approximated by

\[ v_r = Ar_0 \theta_0 \sqrt{\nu/v} \]

for a rotating disk where $A = 0.51023$. The fluid velocity near the electrode surface subjected to an impinging jet is given by (19, 22)

\[ v_r = Br_0 \theta_0 \sqrt{v/a} \]

where $B = 1.312$ and $a$ is a hydrodynamic constant which is proportional to the average jet velocity. Correlations reported for its dependence on the distance between the jet nozzle and the electrode are summarized by Chin and Tsang (20). For either system the equation of convective diffusion can be written in the form

\[ \frac{\partial C}{\partial t} = \frac{1}{3} \frac{\partial^2 C}{\partial z^2} \]

where

\[ \zeta = z \left( \frac{A \nu}{3D_i} \right)^{1/2} \sqrt{\nu/v} \]

for the rotating disk and

\[ \zeta = z \left( \frac{B \nu}{3D_i} \right)^{1/2} \sqrt{v/a} \]

for the impinging jet system. A solution can be obtained for this system by a separation of variables, i.e.

\[ c_r = c_{r,0} \left[ 1 + \sum_{m=0}^{\infty} A_m \left( \frac{r}{r_0} \right)^{2m} \Theta_m(\zeta) \right] \]

where the functions $\Theta_m(\zeta)$ satisfy the differential equation

\[ \Theta_m'' + 3(2m \Theta_m' - 6m \Theta_m) = 0 \]  

subject to the boundary conditions $\Theta_m = 1$ at $\zeta = 0$ and $\Theta_m = 0$ as $\zeta \to \infty$. The concentration at the surface of the disk is therefore given by

\[ c_{r,0} \left[ 1 + \sum_{m=0}^{\infty} A_m \left( \frac{r}{r_0} \right)^{2m} \right] \]

The coefficients $A_m$ are determined by matching the current density obtained from the flux evaluated at the electrode surface

\[ s^i = \frac{D_i}{\partial z} \left[ \Theta_m \right]_{z=0} \]

with the current density obtained from kinetic expressions or to the current density obtained from Ohm's law, also evaluated at the electrode surface, i.e.

\[ \frac{\partial \phi}{\partial z} \left|_{z=0} \right. = -k F \frac{\partial \rho}{\partial r} \]

where the validity of this approach rests upon the assumptions that the diffusion layer is thin, that the current near the electrode is carried only by diffusion of ionic species (valid for an excess of supporting electrolyte), and that the concentration in the outer region is uniform.

The potential in the bulk is obtained by solution of Laplace's equation, $\nabla^2 \phi = 0$, subject to a specified current distribution at the electrode surface, a zero derivative condition on the insulating plane, and a value of zero for the potential infinitely far from the disk. A solution for the electrostatic potential was given by Newman (1) for this system in terms of rotational elliptic coordinates

\[ \Phi = -\frac{RT}{nF} \sum_{k=0}^{\infty} B_k \rho_k(\zeta) M_k(\ell) \]

where

\[ \rho_k = \frac{1}{\sqrt{2k(2k+1)}} \frac{nF}{k=0} B_k P_k(\eta) \]

and $\rho_k(\zeta)$ is the Legendre polynomial of order $2k$. $M_k(\ell)$ is a Legendre function of imaginary argument which satisfies

\[ \frac{d}{d\ell} \left[ (1 + \ell^2) \frac{dM_k}{d\ell} \right] = 2k(2k + 1)M_k \]

with the boundary conditions

\[ M_k = 1 \text{ at } \ell = 0 \text{ and } M_k = 0 \text{ as } \ell \to \infty \]

The potential at the surface of the electrode is therefore given by

\[ \Phi_s = -\frac{RT}{nF} \sum_{k=0}^{\infty} B_k \rho_k(\eta) \]

The potential of the solution adjacent to the electrode also enters into kinetic expressions for the corrosion reaction. A kinetic expression can be chosen for the corrosion of iron which exhibits the mass-transfer limited maximum current, e.g. (3, 4)

\[ \frac{i}{nF} = \frac{k_0}{\alpha \Phi} \left( 1 - \frac{i}{i_{lim}} \right)^{p} \exp \left( \frac{-\alpha \Phi}{RT} (V - \Phi) \right) \]

The anodic reaction given by this expression is presumed to be limited by an unspecified species. Such an expression is consistent with the observed dependence of the limiting current on the square root of hydrodynamic constant. The reaction order $p$ was assumed to be equal to one. Through Eq. [A-11], the effect of mass-transfer limitations to the anodic reaction can be treated without explicit solution of the equation of convective diffusion. Thus, the coefficients $B_k$ can be determined from (4)
coefficients $B_k$ were obtained from Eq. [A-12] [see Law (3) Faraday's constant, 96,487 C/mol].

$i$, local current density, A/cm$^2$

$B = 1.312$

$1.000 \times 10^{-6}$ A/cm$^2$

$2.0$

$\eta$ cathodic transfer coefficient

$\phi_e$ solution potential adjacent to electrode, V

$\Omega$ rotation speed of disk, s$^{-1}$

$\alpha$, anodic transfer coefficient

$\kappa$, anodic rate constant, mol/s $\cdot$ cm$^2$

$\nu$, kinematic viscosity, cm$^2$/s

$\phi_0$, electrical potential, V

$\rho$, density, kg/cm$^3$

APPENDIX B

Solution Technique

Model parameters are presented in Table B-I. The coefficients $B_k$ were obtained from Eq. [A-12] [see Law (3) and Law and Newman (4)]. This step requires an iterative solution. The coefficients $A_m$ were subsequently obtained from Eq. [A-13]. This solution requires values for $\Theta_\alpha(0)$ which were taken from Newman (1). The use of values obtained for a rotating disk system (1, 3, 4) with the exceptions that within the expression for $N_i$ the constant $B$ is replaced by $A$ and the hydrodynamic constant $a$ is replaced by the rotation speed $\Omega$.

Table B-I. Model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodic transfer coefficient</td>
<td>$\alpha_a = 1.0$</td>
</tr>
<tr>
<td>Cathodic transfer coefficient</td>
<td>$\alpha_c = 1.0$</td>
</tr>
<tr>
<td>Reaction order of limiting reactant</td>
<td>$p = 1.0$</td>
</tr>
<tr>
<td>Number of species transferred</td>
<td>$n = 2.0$</td>
</tr>
<tr>
<td>Anodic rate constant</td>
<td>$nFk_a = 1.000 \times 10^6$ A/cm$^2$</td>
</tr>
<tr>
<td>Cathodic rate constant</td>
<td>$nFk_c = 2.078 \times 10^{-6}$ A/cm$^2$</td>
</tr>
<tr>
<td>Bulk solution conductivity</td>
<td>$\kappa = 0.4$ (0 - cm)$^{-1}$</td>
</tr>
</tbody>
</table>

$B_i = \frac{(4k + 1)^{1/2}}{M'_{2k}(0)} \frac{nF^2r_0}{RTx_a} \int_0^1 \gamma(1 - \eta^2)\eta P_{2k}(\eta)d\eta$ [A-12]

The rate of the corrosion reaction (see Eq. [A-11]) is independent of the surface concentration of ferrous ions at the anodic potentials where the salt film is presumed to form. This allows a partial decoupling of the equations such that the $A_m$ coefficients can be obtained from the $B_k$ coefficients through solution of

$B_i = \frac{\pi}{4} \frac{N_i}{s_i} \sum_{m=0}^\infty Q_{k,m}A_m$ [A-13]

where

$Q_{k,m} = \frac{(4k + 1)^{1/2}}{M'_{2k}(0)} \left( \frac{4}{\pi} \right) \Theta_\alpha(0) \int_0^1 \gamma(1 - \eta^2)\eta P_{2k}(\eta)d\eta$

and

$N_i = \frac{r_s}{v} \left( \frac{A}{v} \right)^{1/2} \frac{Bv}{3D_c} \frac{nF^2D_iC_{1,m}}{RTx_a}$

Analogous expressions have been obtained for the rotating disk system (1, 3, 4) with the exceptions that within the expression for $N_i$ the constant $B$ is replaced by $A$ and the hydrodynamic constant $a$ is replaced by the rotation speed $\Omega$.

REFERENCES